

A STUDY OF ELECTRONIC INTERACTIONS IN CERTAIN VINYL ETHERS

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
Chapter	
I. INTRODUCTION	1
Background	1
Statement and Development of the Problem	3
Delineation of Objectives and Methodology	9
Source and Purification of Reagents	13
II. EXPERIMENTAL	14
Preparation of the Compounds	14
Physical Measurements	33
III. DISCUSSION OF RESULTS	64
Preparation of the Compounds	64
Physical Measurements	67
IV. SUMMARY	82
BIBLIOGRAPHY	83
BIOGRAPHICAL SKETCH	86

LIST OF TABLES

Table		Page
1.	TABULATION OF DIPOLE MOMENT DATA	35
2.	TABULATION OF MAXIMA IN ULTRA-VIOLET ABSORPTION SPECTRA	39
3.	TABULATION OF MOLAR REFRACTION DATA FOR VINYLOXY COMPOUNDS	62
4.	TABULATION OF MOLAR REFRACTION DATA FOR ETHYLOXY COMPOUNDS	63
5.	COMPARISON IN YIELDS OF SYNTHETIC METHODS	65

LIST OF FIGURES

Figure		Page
1.	ULTRA-VIOLET ABSORPTION SPECTRA OF 2-VINYLOXY-ETHOXYBENZENE AND 2-ETHYLOXYETHOXYBENZENE	40
2.	ULTRA-VIOLET ABSORPTION SPECTRA OF 2-(2-VINYLOXY)-ETHOXYBENZALDEHYDE AND 2-(2-ETHYLOXY)ETHOXY-BENZALDEHYDE	41
3.	ULTRA-VIOLET ABSORPTION SPECTRA OF 3-(2-VINYLOXY)-ETHOXYBENZALDEHYDE AND 3-(2-ETHYLOXY)ETHOXY-BENZALDEHYDE	42
4.	ULTRA-VIOLET ABSORPTION SPECTRA OF 4-(2-VINYLOXY)-ETHOXYBENZALDEHYDE AND 4-(2-ETHYLOXY)ETHOXY-BENZALDEHYDE	43
5.	ULTRA-VIOLET ABSORPTION SPECTRA OF 2-(2-VINYLOXY)-ETHOXYSTYRENE AND 2-(2-ETHYLOXY)ETHOXYSTYRENE	44
6.	ULTRA-VIOLET ABSORPTION SPECTRUM OF 3-(2-VINYLOXY)-ETHOXYSTYRENE	45
7.	ULTRA-VIOLET ABSORPTION SPECTRA OF 4-(2-VINYLOXY)-ETHOXYSTYRENE AND 4-(2-ETHYLOXY)ETHOXYSTYRENE	46
8.	ULTRA-VIOLET ABSORPTION SPECTRA OF 2-(2-VINYLOXY)-ETHOXY- β -NITROSTYRENE AND 2-(2-ETHYLOXY)ETHOXY- β -NITROSTYRENE	47
9.	ULTRA-VIOLET ABSORPTION SPECTRUM OF 3-(2-ETHYLOXY)-ETHOXY- β -NITROSTYRENE	48
10.	ULTRA-VIOLET ABSORPTION SPECTRA OF 4-(2-VINYLOXY)-ETHOXY- β -NITROSTYRENE AND 4-(2-ETHYLOXY)ETHOXY- β -NITROSTYRENE	49

CHAPTER I

INTRODUCTION

Background

In an attempt to develop a model cross-linking monomer, Butler and Nash (1) first studied ethers containing both vinyl and allyl groups, which were found to undergo polymerization by a sequence of two steps. The first step, giving rise to linear polymers from ethylene glycol vinyl allyl ether and ethylene glycol vinyl crotyl ether, used boron trifluoride etherate as the initiator with toluene as the solvent at -70°C . These investigators then used benzoyl peroxide as the initiator at 65°C . to cross-link the original polymer, obtaining solid polymers, which softened at high temperatures, and which were insoluble in the usual organic solvents. Thus the boron trifluoride etherate initiated polymerization of the vinyl group in the monomer; benzoyl peroxide initiated polymerization of the unreacted allyl groups in the linear polymer.

Next they turned their attention to monomers containing two sites of unsaturation differing very markedly in their reactivity. Such model compounds would be the 2-vinyloxyethoxy- β -nitrostyrenes. In as much as one of the vinyl groups was highly electron deficient (with respect to the vinyl group in ethylene), being directly attached to a nitro group and a

phenyl group, while the other was electron rich (with respect to the same standard), being directly attached to an oxygen atom, it seemed logical that compounds of this type would be ideal for such a study.

Thus the electron deficient double bond should be polymerized by the use of an anionic initiator, such as sodium methoxide, to give a linear, soluble polymer, containing the unreacted vinyloxy groups in the sidechains. Boron trifluoride etherate, which was so successfully employed in past vinyl polymerizations of this same group, would then be used to polymerize these residual vinyloxy groups, producing a cross-linked, insoluble polymer.

Nash (2) reported the preparation of certain of these compounds and found that the electron deficient beta-nitrostyrene group was readily polymerized with sodium methoxide as initiator. However, he also reported that the monomeric 2-vinyloxyethoxy-beta-nitrostyrenes were unreactive towards boron trifluoride etherate, under conditions which lead to the facile polymerization of the standard monomer, vinyl 2-ethylhexyl ether.

In a separate investigation, Butler (3) showed that a series of vinyl ethers all possessed an infrared absorption peak at 8.32 microns (1202 cm^{-1}) and two other carbon-carbon double bond peaks at 6.08 and 6.18 microns (1645 and 1618 cm^{-1}). These compounds were readily polymerized with boron trifluoride etherate to give linear, soluble polymers in which the 8.32 micron peak had disappeared and the 6.08 and 6.18 micron peaks were considerably diminished.

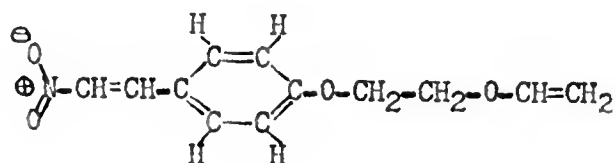
Nash investigated the various isomeric 2-vinyloxyethoxy-benzaldehydes and 2-vinyloxyethoxy- β -nitrostyrenes, and found that all three isomers of this aldehyde possessed these infrared absorption bands, while the 8.32 micron peak was absent in the spectra of the 3- and 4-isomers of the reported beta-nitrostyrenes. As can be anticipated, the three aldehydes could be polymerized with boron trifluoride etherate. In as much as it was not known whether the 8.32 micron peak was attributable to the benzaldehyde moiety (as benzaldehyde also displayed a peak at the same place) or the vinyloxy moiety, no definite conclusions were reached on this point at that time.

Statement and Development of the Problem

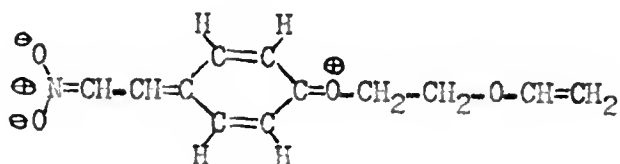
In as much as Nash reported that the vinyl double bond in the vinyloxy group of the beta-nitrostyrenes was not subject to boron trifluoride etherate polymerization, and that the infrared spectra of these compounds did not possess the 8.32 micron peak, the problem immediately suggested itself: are these two facts related to a common cause? If so, what features in the structure of these compounds are responsible for these observations? How can these features, when and if found, be definitely shown to be so responsible?

Taking 4-(2-vinyloxy)ethoxy- β -nitrostyrene as an example, the classical structure of which would be I, one of the most important contributing structures would be II. This would place a fairly strong oxonium ion two (saturated) carbon atoms removed

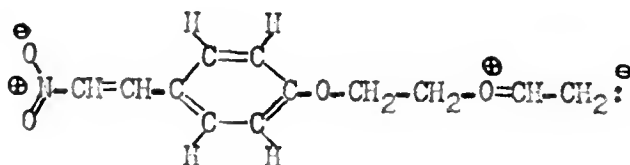
from the oxygen atom of the vinyloxy group. Thus the tendency of one of the unshared pairs of electrons of this oxygen atom, to give rise, via a delocalization process, to a contributing structure such as III would be somewhat diminished by the induction on the part of said oxonium ion across the intervening saturated hydrocarbon bridge.



I



II



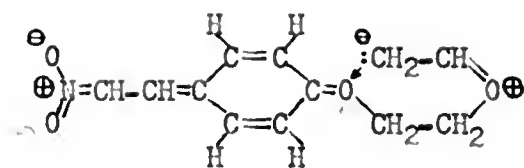
III

To the extent to which a form such as III does not contribute to the structure of the compound, the electron density on the terminal carbon atom of the vinyloxy group would not be augmented by such a delocalization process. Moreover, this resonance effect (+R), to use the terminology of Gould (4), no longer being considered, electrons would be attracted from the double

bond of the vinyloxy group by the inductive effect (-I) of the oxygen atom, and the combination of these two effects would be that the pair of electrons, constituting the pi bond of the vinyloxy group would not be free to coordinate with the empty orbital of the boron atom in the initiator. Since the polymerization proceeds by this form of initiation, this would account for the lack of reactivity of the beta-nitrostyrenes towards boron trifluoride etherate, and hence, their lack of Lewis acid polymerizability. Therefore, since a form such as II does contribute strongly to the structure of the compound, this would seem to explain the experimental data.

Gould (5) states that the pK of chloroacetic acid (chlorine atom inducing across one methylene group) is 2.86, of beta-chloropropionic acid (chlorine atom inducing across a two carbon saturated hydrocarbon bridge) is 4.00, and that of acetic acid is 4.80. Thus it is seen that, while still present, the induction by the chlorine atom in the beta position is quite minor as compared to that in the alpha position. Thus it was felt that the above explanation, relying on the induction of the oxonium ion across a two carbon saturated hydrocarbon bridge, left something to be desired.

Another explanation was devised, wherein the contributing forms, such as II and III are both considered to have important and simultaneous contributions to the structure of the compound, as in IV:



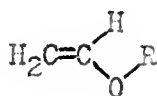
IV

Here, one of the unshared pairs of electrons of the oxygen atom of the vinyloxy group is free to be delocalized and contribute to the extreme form as depicted in III and IV, essentially unhindered by the beta-oxonium ion's weak induction. However, being highly polarized by the nearly positive charge on the phenolic oxonium ion, located six atoms away, it is not free to be donated to the empty orbital of the boron atom in the initiator (or, at least, not as free as is one of the electron pairs on the ethyl ether oxygen atom in the original boron trifluoride etherate complex). To the extent to which this polarization-favored quasi-six-membered ring contributes to the structure of the compound, it could as well explain the experimental observations.

The construction of a model, representative of a form such as IV, shows that such a structure is feasible. Moreover, manipulation of this model lead to the observation that co-planarity between the O-C-C system of the vinyloxy group and the O₂N-C-C-phenyl-O system of the beta-nitrostyryloxy group could be established at the expense of having the two oxygen atoms in the -O-CH₂-CH₂-O- group in the gauche conformation. The slight increase in the energy of the system due to this unfavored conformation would probably be more than overcome by the energy

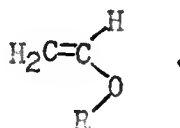
lowering of a pi cloud overlap (even though across an area between two atoms not joined by a sigma bond) which could also extend the pi cloud delocalization.

Shostakovskii (6) postulated a resonance structure for vinyl ethers, for which the rotation of the alkyl group about the C-O bond would be hindered, giving rise to the two rotational isomers:



V

and



VI

The work of Brey (7,8) and Tarrant (8) gave excellent support for this type of isomerism. However, the formation of a ring, as described above, would not allow the existence of both of these isomers. The isomer, similar to the second one depicted (VI), would correspond to IV; the other isomer, similar to the first one depicted (V), would not allow the ring to form. Thus the predictions would be that, based on the above explanation, compounds of the type herein discussed, in whose infrared absorption spectra the 8.32 micron peak is absent, or at least significantly shifted from this value, should not be susceptible to boron trifluoride etherate polymerization and should exhibit only one peak of the two at (about) 6.08 and 6.18 microns.

The method of choice to investigate the above mentioned postulation would be to obtain the infrared spectra of the compounds to be studied. The ultra-violet spectra of those

vinylloxy compounds having a spectral shift in the 8.32 micron peak and only one peak (the 6.18 micron peak) in the 6.08-6.18 micron region should then be compared to the ultra-violet spectra of the corresponding ethylloxy compounds. If such an extension of the pi cloud delocalization does not exist, that is, if there is no interaction between the vinylloxy pi cloud system and the pi cloud system of the beta-nitroethylloxy portion of the molecule, then substitution of the ethylloxy group for the vinylloxy group should lead to the disappearance of only one peak in the ultra-violet spectrum (and then only if the vinylloxy group has an ultra-violet absorption maxima in the range available) and have no change on any others present. On the other hand, if there is an electronic interaction of the type postulated in these vinyl ethers, the substitution of the vinylloxy group by an ethylloxy group should produce a shift in the wavelength and a change in the extinction coefficient of at least one of the maxima present in the spectrum of the vinylloxy compound, and such a shift should be toward shorter wavelength (toward higher energy).

Another method used to investigate the polarization-favored ring would be the determination of the dipole moment and the molar refraction of the various compounds. Structure IV would be expected to have a different dipole moment than either II or III, with III probably having the lowest value, II being intermediate, and IV having the highest value.

If the ring is formed and a form such as IV contributes strongly to the actual structure of the compounds, either by

the polarization-favored mechanism, the extension of pi cloud delocalization, or both, the electronic environment of the beta-hydrogens on the vinyloxy group should be sufficiently altered as to be detectable as a change in the chemical shift of these hydrogen atoms in the nuclear magnetic resonance spectra of these compounds. These determinations are being made by Dr. W. S. Brey and coworkers, and will be reported independently.

Delineation of Objectives and Methodology

The primary objectives of this investigation were the preparation of the compounds and the determination of certain of their physical properties. The secondary objectives were to discover the correlation between these physical properties and the structure of the compounds and to determine if these correlations could be successfully employed in the explanation of the previously reported, experimentally observed behavior of these compounds towards polymerization.

The compounds to be prepared in this investigation were grouped into two series: (a) ethylene glycol substituted-phenyl vinyl ethers, and (b) ethylene glycol substituted-phenyl ethyl ethers. Since the compounds in the second (ethyloxy) series were somewhat similar to those in the first (vinyloxy) series, it was decided, when applicable, to utilize the same methods in their preparation as were employed in the preparation of the compounds of the vinyloxy series.

The compounds to be prepared were: (a) 2-vinyloxyethoxybenzene, 2-, 3-, and 4-(2-vinyloxy)ethoxybenzaldehyde, 2-, 3-, and 4-(2-vinyloxy)-ethoxystyrene, and 2-, 3-, and 4-(2-vinyloxy)-ethoxy- β -nitrostyrene, and (b) 2-ethyloxyethoxybenzene, 2-, 3-, and 4-(2-ethyloxy)ethoxybenzaldehyde, 2-, 3-, and 4-(2-ethyloxy)-ethoxystyrene, and 2-, 3-, and 4-(2-ethyloxy)ethoxy- β -nitrostyrene. The similarity of the two series is apparent.

Butler (3), in the preparation of 2-vinyloxyethoxybenzene, and Nash (2), in the preparation of 2-, 3-, and 4-(2-vinyloxy)-ethoxybenzaldehyde, used essentially the same synthetic procedure: a basic aqueous solution of phenol or the appropriate hydroxybenzaldehyde, prepared in situ by dissolving the phenol in an aqueous potassium hydroxide solution, was treated with 2-chloroethyl vinyl ether. The resulting mixture was heated for some time (usually twenty-four hours), then cooled to room temperature, and extracted with benzene. The benzene solution was then dried and the bulk of the solvent removed by distillation. Fractional distillation of the residual oil gave the desired product.

In the preliminary stages of this investigation these methods of preparation were rechecked with excellent agreement. However, it was felt that the relatively low yield (2-vinyloxyethoxybenzene: 21.0 per cent; 2-(2-vinyloxy)ethoxybenzaldehyde: 31.53 per cent; 3-(2-vinyloxy)ethoxybenzaldehyde: 42.46 per cent; and 4-(2-vinyloxy)ethoxybenzaldehyde: 18.70 per cent) was at least partially due to the hydrolysis of the 2-chloroethyl vinyl ether by either water, present in overwhelming excess, or by an

equilibrium concentration of hydroxide ions. It was thus decided to investigate the feasibility of the isolation of the anhydrous potassium salt of these phenols, then allowing this potassium salt to react with 2-chloroethyl vinyl ether in some non-hydroxylic, inert medium in which they were mutually soluble. The solvent of choice was N,N-dimethylformamide. The results of this phase of the investigation will be discussed under "Discussion of Results."

Nash (2) also reported the preparation of 3- and 4-(2-vinyloxy)-ethoxy- β -nitrostyrene. His reported method of synthesis was rechecked and, indeed, the compounds which were thus obtained showed excellent agreement in melting point with those reported. However, the nuclear magnetic resonance spectra of these compounds, in failing to show the presence of any vinyloxy hydrogen atoms in these compounds, began to cast a serious doubt on the validity of the assignment of the reported structure of these compounds. This doubt lead to the resubmission of these compounds for analysis, in an even purer state on the basis of melting point than that reported: "3-(2-vinyloxy)ethoxy- β -nitrostyrene," m.p.: 113.5-114.0°C. as compared to 112-113°C. and "4-(2-vinyloxy)-ethoxy- β -nitrostyrene," m.p.: 123.5-124.0°C. as compared to 121-122°C. The carbon, hydrogen, and nitrogen analyses of these compounds were in good agreement with the analyses that would be calculated for 3-(2-hydroxy)ethoxy- β -nitrostyrene and 4-(2-hydroxy)-ethoxy- β -nitrostyrene. Thus the final stage in the preparation of these compounds, treatment of the basic condensation reaction

mixture of the appropriate 2-vinyloxyethoxybenzaldehyde, nitromethane, methanol, and aqueous potassium hydroxide solution with excess hydrochloric acid solution lead to the hydrolysis of the vinyl ether. This facile hydrolysis of vinyl ethers is reported in the literature (9-13).

Thus, to the best knowledge of the author, the only compounds included in this investigation that are known to have been previously reported in the chemical literature are 2-vinyloxyethoxybenzene and the 2-, 3-, and 4-(2-vinyloxy)ethoxybenzaldehydes, and these compounds have been prepared by a somewhat different method and in significantly better yields to justify their inclusion in this series of otherwise new, unreported compounds, over and above the fact that they are the intermediates for the corresponding styrenes and beta-nitrostyrenes.

Finally, in as much as these aldehyde intermediates were synthetically available, and since benzaldehyde was known to undergo the Wittig (14) reaction with ease, it was decided to investigate this synthetic route to a new series of potentially interesting monomers. These compounds, being 2-vinyloxyethoxystyrenes, would possess two double bonds of somewhat differing reactivities towards polymerization, and thus may well be ideally constituted for a polymerization study, similar to that conducted by Butler and Nash (cf. Ref. 1). The synthesis of the 2-ethyloxyethoxystyrenes was also investigated, not only due to the fact that they would be interesting monomers for polymerization studies, but also since their physical properties should be

compared to the physical properties of the vinyloxy compounds. Since polymerization studies were outside the scope of this investigation, no such studies were conducted.

Source and Purification of Reagents

Phenol (U. S. P. grade, fused) was obtained from J. T. Baker Chemical Company, Phillipsburg, Pennsylvania, and was used without purification.

2-Hydroxybenzaldehyde (salicylaldehyde, Fisher Reagent Chemical) was obtained from Fisher Scientific Company, Fairlawn, New Jersey, and was used without further purification.

3-Hydroxybenzaldehyde (practical) was obtained from L. Light and Company, Limited, Colnbrook, England, and was used without purification.

4-Hydroxybenzaldehyde (practical) was obtained from Eastman Organic Chemicals Division, Distillation Products Industries, Rochester, New York, and was used without further purification.

Vinyl 2-chloroethyl ether was obtained from Carbide and Carbon Chemicals Company, Union Carbide and Carbon Corporation, New York, New York, and was used without further purification.

2-Bromoethyl ethyl ether (Reagent grade) was obtained from Penninsular Chemresearch, Incorporated, Gainesville, Florida, and was used without any further purification.

Butyl lithium in hexane solution was obtained from Foote Mineral Company, West Chester, Pennsylvania, and was used without purification.

Methyltriphenylphosphonium bromide was obtained from this laboratory and was used without further purification.

CHAPTER II

EXPERIMENTAL

Preparation of the Compounds

A. 2-Vinyloxyethoxybenzene.--This diether was prepared (a) according to the method of Butler (3) and (b) by the method described below.

1. Preparation of the potassium salt.--A solution of 47.06 g. (0.5000 mole) of phenol in 50 ml. of absolute ethanol was added to a solution of 32.74 g. (0.5000 mole) of 85.7 per cent potassium hydroxide in 350 ml. of absolute ethanol. The solvent was removed by distillation; residual moisture was removed by the use of the benzene azeotrope. The lavender, crystalline solid was washed with anhydrous ethyl ether to remove any unreacted phenol, filtered, and dried over calcium sulfate at reduced pressure. Due to the extremely hygroscopic nature of this salt, it was used immediately.

2. Preparation of the diether.--The above potassium salt was dissolved in a solution of 58.60 g. (0.5000 mole plus 10 per cent excess) of 2-chloroethyl vinyl ether in 200 ml. of redistilled dimethylformamide, by stirring on a steam bath. Stirring and heating were continued for ten hours. Upon being cooled to room temperature, the reaction mixture was diluted

with one liter of distilled water and then repeatedly extracted with ethyl ether. The ethereal extracts were dried over anhydrous magnesium sulfate and the bulk of the solvent removed by atmospheric distillation. The residual oil was fractionally distilled under vacuum to give 51.57 g. (62.81 per cent yield) of a clear, colorless liquid, b.p.: 103-105°C./7.5 mm. of mercury. Redistillation of a 46.20 g. sample of this material gave 44.57 g. (96.47 per cent recovery; 60.00 per cent relative over all yield) of a clear, colorless liquid, b.p.: 102-103°C./10 mm. of mercury, n_D^{30} : 1.5152.

Analysis: Calculated for $C_{10}H_{12}O_2$, per cent: C, 73.20; H, 7.32. Found, per cent: C, 73.10; H, 7.43.

B. 2-(2-Vinyloxy)ethoxybenzaldehyde.--This diether was prepared in a manner entirely analogous to that described above.

1. Preparation of the potassium salt.--The potassium salt was prepared on a 1.0000 mole scale by the substitution of salicylaldehyde for the phenol in the previous procedure. The yield of yellow, crystalline solid, after drying to constant weight, was quantitative.

2. Preparation of the diether.--This diether was prepared on a 0.7500 mole scale from 120.0 g. of the potassium salt, 87.9 g. of 2-chloroethyl vinyl ether, and 500 ml. of redistilled dimethylformamide, by the procedure cited above. Fractional distillation of this product gave 106.61 g. (73.95 per cent yield) of a clear, colorless liquid, b.p.: 101-103°C./0.1 mm. of mercury; n_D^{30} : 1.5427.

Analysis: Calculated for $C_{11}H_{12}O_3$, per cent: C, 68.73; H, 6.29. Found, per cent: C, 68.43; H, 6.25.

C. 3-(2-Vinyloxy)ethoxybenzaldehyde.--With the exception of a slight modification in the preparation of the potassium salt, this diether was prepared in the same manner as cited above.

1. Preparation of the potassium salt.--This potassium salt was prepared on a 0.3000 mole scale by adding 19.65 g. of 85.75 potassium hydroxide dissolved in 150 ml. of absolute ethanol to a solution of 36.64 g. of m-hydroxybenzaldehyde in 150 ml. of absolute ethanol cooled to the vicinity of 5°C. Heat was not supplied during the vacuum distillation used to remove the solvent. After being washed with anhydrous ethyl ether to remove any unreacted m-hydroxybenzaldehyde, filtered, and dried, the yield of greenish yellow, crystalline solid was 47.00 g. (97.77 per cent yield).

2. Preparation of the diether.--This diether was prepared in the same manner as described above from 47.00 g. (0.2934 mole) of the potassium salt, 42.63 g. (0.2934 mole plus 36.4 per cent excess) of 2-chloroethyl vinyl ether, and 250 ml. of redistilled dimethylformamide. Fractional distillation of the crude product gave 46.31 g. (82.11 per cent yield) of a clear, colorless liquid, b.p.: 106-107°C./0.50 mm. of mercury; n_D^{19} : 1.5470. This is the material referred to as the "liquid modification."

Analysis: Calculated for $C_{11}H_{12}O_3$, per cent: C, 68.73; H, 6.29. Found, per cent: C, 68.57; H, 6.47.

By the low temperature removal of solvent by reduced pressure distillation of a small amount of a benzene solution of the "liquid modification," a solid was produced. This solid was used to seed a 15.98 g. sample of the "liquid modification," resulting in the crystallization of a total of 13.48 g. (84.36 per cent yield) of a white, crystalline solid, m.p.: 39.0-40.5°C. Recrystallization of a 10.00 g. sample of this solid from pentane gave 7.75 g. (77.5 per cent recovery) of a white, crystalline solid, m.p.: 41.0-42.0°C. This is the material referred to as the "solid modification."

Analysis: Calculated for $C_{11}H_{12}O_3$, per cent: C, 68.73; H, 6.29. Found, per cent: C, 68.89; H, 6.27.

D. 4-(2-Vinyloxy)ethoxybenzaldehyde.--This diether was prepared in the same manner as 2-(2-Vinyloxy)ethoxybenzaldehyde, described above.

1. Preparation of the potassium salt.--The potassium salt was prepared in quantitative yield on a 0.5000 mole scale from 61.06 g. of p-hydroxybenzaldehyde and 32.75 g. of 85.7 per cent potassium hydroxide.

2. Preparation of the diether.--This diether was prepared on 0.5000 mole scale from 80.11 g. of the potassium salt, 53.28 g. of 2-chloroethyl vinyl ether, and 200 ml. of redistilled dimethylformamide. Distillation of the crude product gave 79.28 g. (82.49 per cent yield) of clear, light tan liquid, b.p.: 133-140°C./1.1 mm. of mercury. As the liquid crystallized on the refractometer platform, the index of refraction could not

be determined; however, this solid material was used to seed the liquid. In this manner a total of 77.59 g. (97.87 per cent recovery; 80.74 per cent over all yield) of a light tan, crystalline solid, m.p.: 39.5-40.5°C., was obtained. Recrystallization failed to change the melting point, but did give a white, crystalline solid.

Analysis: Calculated for $C_{11}H_{12}O_3$, per cent: C, 68.73; H, 6.29. Found, per cent: C, 68.95; H, 6.38.

E. 2-(2-Vinyloxy)ethoxystyrene.--This styrene was prepared by the Wittig (14) reaction from the methylene ylid (prepared in situ) and the previously prepared 2-(2-vinyloxy)ethoxybenzaldehyde.

1. Preparation of the methylene ylid.--Dry nitrogen gas was passed over a vigorously stirred slurry of 89.31 g. (0.2500 mole) of methyltriphenylphosphonium bromide in one liter of anhydrous ethyl ether for one hour at room temperature. Then 188 ml. of a 14.90 per cent solution of butyl lithium in hexane was slowly added by means of a hypodermic syringe. After an additional 30 minutes of stirring, the yellow reaction mixture was nearly clear.

2. Preparation of the styrene.--A solution of 48.06 g. (0.2500 mole) of 2-(2-vinyloxy)ethoxybenzaldehyde in 250 ml. of anhydrous ethyl ether was slowly added with constant stirring to the above reaction mixture. The white slurry was then stirred overnight. After the addition of one liter of distilled water to the reaction mixture and stirring for a short time, the two phases were separated. The aqueous phase was repeatedly

extracted with ethyl ether. These ethereal extracts were combined with the original ethereal phase and the whole was extracted with water, then dried over anhydrous magnesium sulfate. Removal of the bulk of the solvent by a reduced pressure distillation gave a thick, semi-solid oil, which was repeatedly extracted with petroleum ether. Again, the bulk of the solvent was removed by reduced pressure distillation. The residual oil was fractionally distilled under vacuum to give 22.26 g.

(46.80 per cent yield) of a clear, colorless liquid, b.p.: 85-89°C./0.50 mm. of mercury; n_D^{19} : 1.5480-1.5485. Redistillation of 20.00 g. of this material gave 15.53 g. (77.65 per cent recovery; 36.34 per cent relative over all yield) of a clear, colorless liquid, b.p.: 90-91°C./0.70 mm. of mercury; $n_D^{27.5}$: 1.5441.

Analysis: Calculated for $C_{12}H_{14}O_2$, per cent: C, 75.76; H, 7.42. Found, per cent: C, 75.68; H, 7.20.

F. 3-(2-Vinyloxy)ethoxystyrene.--This styrene was prepared in exactly the same manner as described above.

1. Preparation of the methylene ylid.--The methylene ylid was prepared in exactly the same manner as described above, but on a 0.1000 mole scale, from 35.73 g. of methyltriphenylphosphonium bromide, 90 ml. of a 15.04 per cent solution of butyl lithium in hexane, and 350 ml. of anhydrous ethyl ether.

2. Preparation of the styrene.--This styrene was prepared as described above, but on a 0.1000 mole scale. Distillation of the crude production gave 8.46 g. (44.48 per cent yield) of a clear, colorless liquid, 89-114°C./0.08 mm. of mercury;

n_D^{30} : 1.5325-1.5410. Combination of this material and that produced by a subsequent synthesis to give a starting charge of 17.00 g. and redistillation gave a total of 12.10 g. (71.18 per cent recovery; 31.80 per cent relative over all yield) of a clear, colorless liquid, b.p.: 79-84°C./0.06 mm. of mercury; n_D^{30} : 1.5435.

Analysis: Calculated for $C_{12}H_{14}O_2$, per cent: C, 75.76; H, 7.42. Found, per cent: C, 75.85; H, 7.47.

G. 4-(2-Vinyloxy)ethoxystyrene.--This styrene was prepared in an analogous manner to that described above, but was purified differently.

1. Preparation of the methylene ylid.--The methylene ylid was prepared exactly as described above on a 0.2000 mole scale from 71.45 g. of methyltriphenylphosphonium bromide, 150 ml. of a 15.04 per cent solution of butyl lithium in hexane, and 750 ml. of anhydrous ethyl ether.

2. Preparation of the styrene.--The same procedure, as described above, was followed up to the point of the reduced pressure distillation of the petroleum ether solvent. At this point, instead of a residual oil, 28.00 g. (72.82 per cent yield) of a waxy, white solid was obtained. This material melted (m.p.: 54-56°C.) to give a cloudy melt, suggesting the presence of triphenylphosphine oxide as an impurity. Chromatographic purification over an activated alumina column, followed by recrystallization of the product, gave a total of 19.14 g. (68.35 per cent recovery; 49.77 per cent over all yield) of

lustrous, white flakes, m.p.: 59.5-60.5°C.

Analysis: Calculated for $C_{12}H_{14}O_2$, per cent: C, 75.76; H, 7.42. Found, per cent: C. 75.59; H. 7.19.

H. 2-(2-Vinyloxy)ethoxy- β -nitrostyrene.--Fundamentally these compounds were made according to the method of Thiele (15), with slight modifications, as described below. A solution of 48.05 g. (0.2500 mole) of 2-(2-vinyloxy)ethoxybenzaldehyde, 15.26 g. (0.2500 mole) of redistilled nitromethane, and 250 ml. of methanol was cooled in an ice bath to the vicinity of 5°C. with constant stirring. A solution of 16.37 g. (0.2500 mole) of 85.7 per cent potassium hydroxide in 50 ml. of distilled water and 100 ml. of methanol was added dropwise, at such a rate that the temperature of the reaction mixture did not rise above 5°C. The clear, greenish yellow solution was then poured over 250 g. of ice in a separatory funnel and the resulting white mixture was slowly poured into a vigorously stirred mixture of 22.5 ml. of concentrated hydrochloric acid solution, 250 g. of ice, and 250 ml. of cold, distilled water. The yellow precipitate was filtered under suction, immediately washed with two liters of cold, distilled water, and then with one liter of distilled water at room temperature, and then sucked air dry. A total of 53.23 g. (90.51 per cent yield) of yellow powder, m.p.: 56-58°C., was obtained.

Recrystallization of a 25.00 g. sample of this material from methanol gave a total of 15.00 g. (60.00 per cent recovery; 54.31 per cent relative over all yield) of a fine, yellow,

crystalline solid, m.p.: 62.0-62.5°C. Subsequent recrystallizations failed to change the melting point.

Analysis: Calculated for $C_{12}H_{13}NO_4$, per cent: C, 61.27; H, 5.95. Found, per cent: C, 61.44; H, 5.71; N, 5.91

I. 3-(2-Vinyloxy)ethoxy-8-nitrostyrene.--Despite repeated attempts to synthesize this compound, either using exactly the procedure developed for the successful synthesis of 2-(2-vinyloxy)-ethoxy-8-nitrostyrene, or modifications in addition rate, addition time, or addition order, no successful synthesis for this compound has as yet been developed.

J. 4-(2-Vinyloxy)ethoxy-8-nitrostyrene.--The procedure developed for the above synthesis was successful for the synthesis of this compound from 19.23 g. (0.1000 mole) of 4-(2-vinyloxy)-ethoxybenzaldehyde, 6.11 g. (0.1000 mole) of redistilled nitromethane, and 125 ml. of methanol, with a basic solution of 6.55 g. (0.1000 mole) of 85.7 per cent potassium hydroxide dissolved in 20 ml. of water and 40 ml. of methanol, and an acidic solution of 9.0 ml. of concentrated hydrochloric acid solution, 100 g. of ice, and 100 ml. of cold distilled water. The product obtained was a yellow powder, m.p.: 107-108°C., with a yield of 12.70 g. (53.97 per cent). Recrystallization from absolute ethanol gave 9.50 g. (74.85 per cent recovery; 40.40 per cent over all yield) of bright yellow crystals, m.p.: 108.0-108.5°C.

Analysis: Calculated for $C_{12}H_{13}NO_4$, per cent: C, 61.27; H, 5.57; N, 5.95. Found, per cent: C, 61.21; H, 5.51; N, 5.95.

K. 2-Ethyloxyethoxybenzene.--This diether was prepared in the same manner as 2-vinyloxyethoxybenzene.

1. Preparation of the potassium salt.--A solution of 13.53 g. (0.2500 mole) of phenol in 50 ml. of absolute ethanol was added to a solution of 16.37 g. (0.2500 mole) of 85.7 per cent potassium hydroxide in 100 ml. of absolute ethanol. The solvent was removed by distillation at reduced pressure; residual moisture was removed by the use of the benzene azeotrope. The lavender, crystalline solid was washed with ethyl ether, then dried over calcium sulfate under reduced pressure. The yield of dry salt was 30.45 g. (99.67 per cent).

2. Preparation of the diether.--The above potassium salt was dissolved in a solution of 42.10 g. (0.2500 mole plus 10 per cent excess) of 2-bromoethyl ethyl ether in 150 ml. of redistilled dimethylformamide by stirring on a steam bath. Stirring and heating were continued for ten hours. Upon being cooled to room temperature, the reaction mixture was diluted with one liter of distilled water and repeatedly extracted with ethyl ether. The ethereal extracts were dried over anhydrous magnesium sulfate and the bulk of the solvent removed by atmospheric distillation. The residual oil was fractionally distilled under vacuum to give 18.81 g. (45.26 per cent yield) of a clear, colorless liquid, b.p.: 101-102°C./7.0 mm. of mercury; n_D^{30} : 1.4958-1.4967. Redistillation gave 12.45 g. (66.19 per cent recovery; 29.96 per cent over all yield) of a clear, colorless liquid, b.p.: 101-102°C./7.5 mm. of mercury; n_D^{30} : 1.4960; d^{30} : 0.9971 g./ml.

Analysis: Calculated for $C_{10}H_{14}O_2$, per cent: C, 72.26; H, 8.49. Found, per cent: C, 72.07; H, 8.42.

L. 2-(2-Ethyloxy)ethoxybenzaldehyde.--This diether was prepared in a manner analogous to that used in the preparation of 2-(2-vinyloxy)ethoxybenzaldehyde.

1. Preparation of the potassium salt.--A solution of 122.12 g. (1.0000 mole) of salicylaldehyde in 50 ml. of 95 per cent ethanol was slowly added to a solution of 65.48 g. (1.0000 mole) of 85.7 per cent potassium hydroxide in 350 ml. of 95 per cent ethanol, with stirring in an ice bath. The yellow potassium salt was removed by filtration, washed with pentane, and then ethyl ether. A large amount of ethyl ether was added to the filtrate and the resulting mixture was filtered and washed with ethyl ether. The crops of potassium salt were combined and dried at reduced pressure. The yield (160.2 g.) was quantitative.

2. Preparation of the diether.--A solution of 40.05 g. (0.2500 mole) of the potassium salt in 42.09 g. (0.2500 mole plus 10 per cent excess) of 2-bromoethyl ethyl ether and 150 ml. of redistilled dimethylformamide was heated on the steam bath for ten hours with constant stirring. Upon being cooled to room temperature, the reaction mixture was diluted with 600 ml. of distilled water, then repeatedly extracted with ethyl ether. The ethereal extracts were dried over anhydrous magnesium sulfate and were then reduced to a small volume of residual oil by the atmospheric distillation of the solvent. Fractional distillation

of the residual oil under vacuum gave 40.26 g. (82.91 per cent yield) of a clear, light yellow liquid, b.p.: 94-98°C/0.08 mm. of mercury; n_D^{30} : 1.5225. Combination of this material and that from a subsequent run and redistillation gave a total of 69.50 g. of a clear, colorless liquid (from a starting charge of 104.80 g.), a recovery of 66.32 per cent and a relative over all yield of 54.99 per cent; b.p.: 115-116°C./1.0 mm. of mercury; n_D^{30} : 1.5250; d^{30} : 1.0785 g./ml.

Analysis: Calculated for $C_{11}H_{14}O_3$, per cent: C, 68.02; H, 7.27. Found, per cent: C, 67.93; H, 7.23.

M. 3-(2-Ethyloxy)ethoxybenzaldehyde.--This diether was prepared in a manner analogous to that used for 3-(2-vinyloxy)-ethoxybenzaldehyde.

1. Preparation of the potassium salt.--A solution of 16.37 g. (0.2500 mole) of 85.7 per cent potassium hydroxide in 100 ml. of 95 per cent ethanol was added to a solution of 30.53 g. (0.2500 mole) of *m*-hydroxybenzaldehyde in 100 ml. of 95 per cent ethanol and the resulting solution was evaporated to dryness under vacuum without the application of heat. The light brown, crystalline solid was not isolated, but was immediately used for the next step.

2. Preparation of the diether.--The potassium salt was dissolved in a solution of 38.26 g. (0.2500 mole) of 2-bromoethyl ethyl ether in 200 ml. of redistilled dimethylformamide. This solution was heated on the steam bath with constant stirring for five hours. The reaction mixture was cooled to room temperature

and diluted with one liter of distilled water. This mixture was repeatedly extracted with ethyl ether. The ethereal extracts were dried over anhydrous magnesium sulfate, then were reduced in volume to a residual oil by the atmospheric distillation of the solvent. Fractional distillation of this oil under vacuum gave 31.42 g. (64.72 per cent yield) of a clear, colorless liquid, b.p.: 114-118°C./0.80 mm. of mercury; n_D^{30} : 1.5182-1.5228. Redistillation of 50.00 g. of a combination of this material and that from a subsequent run gave 48.06 g. (96.12 per cent recovery; 62.21 per cent relative over all yield) of a clear, colorless liquid, b.p.: 104-105°C./0.5 mm. of mercury; n_D^{30} : 1.5234; d^{30} : 1.0799 g./ml.

Analysis: Calculated for $C_{11}H_{14}O_3$, per cent: C, 68.02; H, 7.27. Found, per cent: C, 67.86; H, 7.48.

N. 4-(2-Ethoxy)ethoxybenzaldehyde.--This diether was also prepared in a manner similar to that used for the corresponding vinyloxy compound, but was purified by distillation.

1. Preparation of the potassium salt.--A solution of 65.48 g. (1.000 mole) of 85.7 per cent potassium hydroxide in 250 ml. of 95 per cent ethanol was added to a solution of 122.12 g. (1.000 mole) of p-hydroxybenzaldehyde in 250 ml. of 95 per cent ethanol. The solvent was removed on the steam bath under reduced pressure. The lavender solid was ground to a powder, washed with anhydrous ethyl ether, filtered, and dried. The yield was quantitative.

2. Preparation of the diether.--The potassium salt was dissolved in a solution of 153.03 g. (1.000 mole) of 2-bromoethyl

ethyl ether in 500 ml. of redistilled dimethylformamide. The solution was heated on the steam bath with constant stirring for ten hours. After cooling to room temperature, the reaction mixture was diluted with 3 liters of distilled water, and then repeatedly extracted with ethyl ether. The ethereal extracts were dried over anhydrous magnesium sulfate and then reduced in volume to a residual oil by the atmospheric distillation of the solvent. Fractional distillation of this residual oil under vacuum gave 153.17 g. (78.86 per cent yield) of a clear, pink liquid, b.p.: 128-130°C./1.4 mm. of mercury; n_D^{30} : 1.5389-1.5409. Redistillation of a 152.00 g. sample of this material gave 128.38 g. (82.48 per cent recovery; 64.56 per cent relative over all yield) of a clear, colorless liquid, b.p.: 127-128°C./1.2 mm. of mercury; n_D^{30} : 1.5401; d^{30} : 1.0866 g./ml.

Analysis: Calculated for $C_{11}H_{14}O_3$, per cent: C, 68.02; H, 7.27. Found, per cent: C, 67.86; H, 7.27.

0. 2-(2-Ethyloxy)ethoxystyrene.--This styrene was prepared in the same manner as the corresponding vinyloxy compound.

1. Preparation of the methylene ylid.--Dry nitrogen gas was passed over a vigorously stirred slurry of 71.45 g. (0.2000 mole) of methyltriphenylphosphonium bromide in 500 ml. of anhydrous ethyl ether for 30 minutes. With the system still under nitrogen sweep, 180 ml. (0.2000 mole plus 44 per cent excess) of a solution of 14.95 per cent butyl lithium in hexane was slowly added by means of a hypodermic syringe. After an additional 30 minutes of stirring under nitrogen sweep, the solution was nearly clear.

2. Preparation of the styrene.--A solution of 38.48 g. (0.1981 mole) of 2-(2-ethyloxy)ethoxybenzaldehyde in 100 ml. of anhydrous ethyl ether was added dropwise. After an additional 30 minutes of stirring, 250 ml. of water was added and stirring was continued until two definite phases were detected and no more gas was evolved. The ethereal layer was separated and the aqueous layer was extracted with ethyl ether. The ethereal solutions were combined, back-extracted with water, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent by reduced pressure distillation gave a residual oil, which was fractionally distilled under vacuum to give 12.45 g. (32.69 per cent yield) of a clear, colorless liquid, b.p.: 69-72°C./0.03 mm. of mercury; n_D^{30} : 1.5245.

Analysis: Calculated for $C_{12}H_{16}O_2$, per cent: C, 74.97; H, 8.39. Found, per cent: C, 74.89; H, 8.56.

P. 3-(2-Ethyloxy)ethoxystyrene.--This styrene was prepared in the same manner as the corresponding vinyloxy compound.

1. Preparation of the methylene ylid.--Dry nitrogen gas was passed over a vigorously stirred slurry of 26.87 g. (75.2 millimoles) of methyltriphenylphosphonium bromide in 300 ml. of anhydrous ethyl ether for 15 minutes. With the system still under nitrogen sweep, 50 ml. (80.0 millimoles; 75.2 millimoles plus 6.38 per cent excess) of a 14.95 per cent solution of butyl lithium in hexane was slowly added by means of a hypodermic syringe. After an additional 15 minutes of stirring under nitrogen sweep, the reaction mixture was nearly clear.

2. Preparation of the styrene.--A solution of 14.60 g. (75.2 millimoles) of 3-(2-ethyloxy)ethoxybenzaldehyde in 100 ml. of anhydrous ethyl ether was then added dropwise to the above reaction mixture. After two hours of additional stirring, 200 ml. of distilled water was added and stirring was continued until two definite phases were detected and no more gas was evolved. The aqueous phase was separated from the ethereal phase and was repeatedly extracted with ethyl ether. These ethereal extracts were combined with the original ethereal phase. This ethereal solution was extracted with water, dried over anhydrous magnesium sulfate, and reduced in volume to a residual oil by the reduced pressure distillation of the solvent. Fractional distillation of this residual oil under vacuum gave 9.65 g. (66.74 per cent yield) of a clear, colorless liquid, b.p.: 90-92°C./0.10 mm. of mercury; n_D^{30} : 1.5240.

The infrared absorption spectrum and the nuclear magnetic resonance spectrum of this material indicated the presence of the unreacted starting aldehyde. Up to the time of this writing, no satisfactory method for the separation of the styrene from the aldehyde, for the destruction of the aldehyde, or for the complete conversion of the unreacted aldehyde into product styrene has been developed. This problem is under active investigation at the present time.

Analysis: Calculated for $C_{12}H_{16}O_2$, per cent: C, 74.97; H, 8.29. Found, per cent: C, ; H, .

Q. 4-(2-Ethyloxy)ethoxystyrene.--This styrene was prepared in a manner similar to that used for the synthesis of the vinyloxy compound.

1. Preparation of the methylene ylid.--This non-isolated intermediate was prepared on a 0.1000 mole scale in the manner previously used from 35.72 g. of methyltriphenylphosphonium bromide, 400 ml. of anhydrous ethyl ether, and 90 ml. of a 14.95 per cent solution of butyl lithium in hexane.

2. Preparation of the styrene.--The procedure, used for the successful synthesis of 2-(2-ethyloxy)ethoxystyrene, was followed, using the above methylene ylid solution and a solution of 19.42 g. (0.1000 mole) of 4-(2-ethyloxy)ethoxybenzaldehyde in 100 ml. of anhydrous ethyl ether, followed by three liters of distilled water. Fractional distillation of the residual oil under vacuum gave 8.19 g. (42.59 per cent yield) of a clear, colorless liquid, b.p.: 103-105°C/1.1 mm. of mercury; n_D^{30} : 1.5315. An infrared absorption spectrum and a nuclear magnetic resonance spectrum of this material showed that there was no detectable amount of contamination with unreacted aldehyde.

Analysis: Calculated for $C_{12}H_{16}O_2$, per cent: C, 74.97; H, 8.39. Found, per cent: C. 74.92; H, 8.49.

R. 2-(2-Ethyloxy)ethoxy-8-nitrostyrene.--A solution of 19.42 g. (0.1000 mole) of 2-(2-ethyloxy)ethoxybenzaldehyde, 6.10 g. (0.1000 mole) of redistilled nitromethane, and 100 ml. of methanol was cooled in an ice bath with constant stirring

to the vicinity of 5°C. Then 100 ml. of a 1.00 N aqueous solution of potassium hydroxide was added at such a rate that the temperature of the reaction mixture did not exceed 10°C. Poured over 100 g. of ice in a separatory funnel, this cloudy mixture was slowly added to a constantly stirred mixture of 100 ml. of a 1.00 N aqueous hydrochloric acid solution and 200 g. of ice. Filtration of the resulting thick, yellow suspension, followed by washing with cold distilled water, and suction drying, gave 16.32 g. (68.77 per cent yield) of a yellow powder, m.p.: 35-35°C. Recrystallization from methanol gave 11.22 g. (68.75 per cent recovery; 47.28 per cent over all yield) of yellow crystals, m.p.: 37.0-38.0°C. A final recrystallization of this material gave a total of 11.00 g. (98.04 per cent recovery; 46.35 per cent over all yield) of yellow crystals, m.p.: 38.0-38.5°C.

Analysis: Calculated for $C_{12}H_{15}NO_4$, per cent: C, 60.75; H, 6.37; N, 5.90. Found, per cent: C, 60.63; H, 6.50; N, 5.92.

S. 3-(2-Ethyloxy)ethoxy-β-nitrostyrene.--After cooling a solution of 19.42 g. (0.1000 mole) of 3-(2-ethyloxy)ethoxybenzaldehyde, 6.10 g. (0.1000 mole) of nitromethane, and 100 ml. of methanol to the vicinity of 5°C. in ice with constant stirring, 100 ml. of a 1.00 N aqueous solution of potassium hydroxide was added at such a rate that the temperature of the reaction mixture did not exceed 10°C. The yellow solution was poured over 100 g. of ice in a separatory funnel, then added drop by drop to a mixture of 100 ml. of a 1.00 N aqueous hydrochloric acid solution and 100 g. of ice, vigorous manual stirring being employed throughout the

addition. The thick, yellow slurry was then filtered, washed with cold water, and dried by suction. After drying over anhydrous calcium sulfate under vacuum overnight, the yield of dry, yellow powder was 19.00 g. (83.59 per cent yield), m.p.: 36-39°C. Recrystallization from methanol gave a total of 13.35 g. (70.26 per cent recovery; 56.26 per cent over all yield) of yellow flakes, m.p.: 43.0-44.0°C. A final recrystallization from a 50-50 mixture of ethyl ether and pentane gave 12.00 g. (96.78 per cent recovery; 50.57 per cent over all yield) of yellow, crystalline material, m.p.: 44.5-45.0°C.

Analysis: Calculated for $C_{12}H_{15}NO_4$, per cent: C, 60.75; H, 6.37; N, 5.90. Found, per cent: C, 60.64; H, 6.24; N, 5.91.

T. 4-(2-Ethoxy)ethoxy-8-nitrostyrene. --After a solution of 19.42 g. (0.1000 mole) of 4-(2-ethoxy)ethoxybenzaldehyde, 6.10 g. (0.1000 mole) of nitromethane, and 100 ml. of methanol was cooled in an ice bath with constant stirring to the vicinity of 5°C., 100 ml. of a 1.00 N aqueous solution of potassium hydroxide was added at such a rate that the temperature of the reaction mixture did not exceed 10°C. The reaction mixture was then poured over 100 g. of ice in a separatory funnel, then added with vigorous manual stirring to a mixture of 100 ml. of a 1.00 N aqueous hydrochloric acid solution and 100 g. of ice. The resulting yellow slurry was filtered, washed with cold water, and sucked air dry. A total of 16.35 g. (68.82 per cent yield) of yellow powder, m.p.: 55-65°C., was thus obtained. Recrystallization of this material from methanol gave a total of 9.71 g.

(59.46 per cent recovery; 41.21 per cent over all yield) of fine, yellow needles, m.p.: 74.0-74.5°C.

Analysis: Calculated for $C_{12}H_{15}NO_4$, per cent: C, 60.75; H, 6.37; N, 5.90. Found, per cent: C, 60.82; H, 6.45; N, 5.89.

Physical Measurements

A. Dipole Moment Measurement.--The method of Popov and Holm (16) was used exclusively. Briefly, this consisted of making up solutions of varying concentrations on a weight/weight basis for each of the desired compounds in benzene (or dioxane) and determining the dielectric constant, the specific volume, and the square of the index of refraction for each of the solutions. These values were then plotted against the weight fraction of solute, W_2 , for each solution. The best straight line was then drawn through these experimental points and extrapolated to infinite dilution ($W_2 = 0$). Determination of the intercept and the slope of the line for each of the three above-mentioned determinations gave, respectively, the values ϵ_1 and α , ν_1 and β , $[(n_D^{30})_1]^2$ and γ . These quantities were used to determine the quantities $P_{2\infty}$ and P_M , the polarization of the solute at infinite dilution and the molar refraction, respectively, by the relations:

$$P_{2\infty} = \frac{M_2}{(\epsilon_1 + 2)} \left[\frac{3\alpha\nu_1}{(\epsilon_1 + 2)} + (\nu_1 + \beta)(\epsilon_1 - 1) \right]$$

$$P_M = \frac{M_2}{((n_{D1}^{30})^2 + 2)} \left[\frac{3\gamma}{((n_{D1}^{30})^2 + 2)} + (\nu_1 + \beta)(n_{D1}^{30})^2 - 1 \right] .$$

These quantities, in turn, were used in the determination of μ , the dipole moment, by the expression:

$$\mu = (0.2230)(P_{2\infty} - P_M)^{1/2}.$$

A rigorously purified sample of anisole was used to determine the accuracy of the method. The experimental data are tabulated in Table 1.

1. Purification of the solvents:

a. Benzene.--The benzene used was Phillips "Pure Grade, 99 mole per cent minimum." This was dried and fractionally distilled over sodium ribbon. The distillate boiling at ambient pressure between 80-81°C. was collected, and cooled three-fourths of the sample was frozen. The crystals were isolated by decantation, and were allowed to melt. The melt was stored over sodium ribbon and redistilled immediately before use.

b. 1,4-Dioxane.--The dioxane used was Matheson, Coleman, and Bell's "Spectroquality Reagent" grade. This was dried over calcium hydride, filtered, and distilled at ambient pressure over anhydrous calcium sulfate. The distillate boiling between 100.5-101.5°C. was collected, and cooled until three-fourths of the sample was frozen. From this point on, it received the same treatment as described above.

2. Apparatus used:

a. Capacitance cell.--The capacitance cell was supplied by Balsbaugh Laboratories and was a modified type 2TN25, having a determined capacitance at 30.0°C. of 24.53 micromicrofarads, at a frequency of 10 kc.

TABLE 1
TABULATION OF DIPOLE MOMENT DATA

Compound	ϵ_1	α	ν_1	β	$(n_D^{30})^2$	γ	$P_{2\infty}$	R_M	$\mu(D)$
Anisole	2.2400	1.5625	1.15342	-0.15600	2.23382	0.05500	64.06	32.58	1.25
2-Vinyloxyethoxy- benzene	2.2325	2.0625	1.15155	-0.18000	2.23436	0.05750	111.77	48.33	1.78
2-(2-Vinyloxy)ethoxy- benzaldehyde	2.2200	12.0000	1.15200	-0.26133	2.23375	0.14000	497.13	55.08	4.69
3-(2-Vinyloxy)ethoxy- benzaldehyde*	2.2625	5.5000	1.15125	-0.26300	2.233425	0.12200	251.53	54.26	3.13
4-(2-Vinyloxy)ethoxy- benzaldehyde	2.2310	9.21438	1.15200	-0.26923	2.23412	0.18261	391.30	56.22	4.08
2-(2-Vinyloxy)ethoxy- styrene	2.2715	2.0300	1.15114	-0.1790	2.23425	0.1422	128.18	59.14	1.85
3-(2-Vinyloxy)ethoxy- styrene	2.2568	2.6440	1.15113	-0.18900	2.233325	0.13750	149.90	58.37	2.13
4-(2-Vinyloxy)ethoxy- styrene	2.2656	2.7000	1.15157	-0.19750	2.23260	0.1583	151.38	58.66	2.15
2-(2-Vinyloxy)ethoxy- β -nitrostyrene**	2.2030	17.6667	0.97751	-0.14000	2.00983	0.39000	746.31	66.35	5.81

*Liquid modification.

**1,4-Dioxane used as solvent; benzene used as solvent on all others.

TABLE 1---Continued

Compound	ϵ_1	α	ν_1	β	$(n_D^{20})^2$	γ	$P_{2\infty}$	R_M	$\mu(D)$
4-(2-Vinyloxy)ethoxy- β -nitrostyrene*	2.2040	15.5556	0.97900	-0.15645	2.00931	0.52800	663.46	71.40	5.43
2-Ethylxoyethoxy- benzene	2.2525	2.3200	1.15277	-0.14500	2.23309	0.03591	123.09	49.95	1.91
2-(2-Ethylxoy)ethoxy- benzaldehyde	2.2490	11.0000	1.15138	-0.23200	2.23381	0.07875	461.27	54.99	4.49
3-(2-Ethylxoy)ethoxy- benzaldehyde	2.2540	6.5000	1.15275	-0.23000	2.23464	0.06560	294.10	54.71	3.45
4-(2-Ethylxoy)ethoxy- benzaldehyde	2.2550	11.0000	1.15147	-0.24250	2.23367	0.12075	459.72	55.97	4.48
2-(2-Ethylxoy)ethoxy- styrene	2.2579	2.7000	1.15288	-0.15357	2.23443	0.09750	155.79	59.63	2.19
4-(2-Ethylxoy)ethoxy- styrene	2.2517	2.4500	1.15270	-0.14400	2.23294	0.10375	147.20	60.34	2.08
2(2-Ethylxoy)ethoxy- β -nitrostyrene	2.1985	16.6250	0.97736	-0.10200	2.00762	0.50000	715.39	73.88	5.65

* 1,4-Dioxane used as solvent; benzene used as solvent on all others

TABLE 1--Continued

Compound	ϵ_1	α	ν_1	β	$(n_D^{30})^2$	γ	P_{20}	R_M	$\mu(D)$
3-(2-Ethoxy)ethoxy- β -nitrostyrene*	2.1980	15.0000	0.97881	-0.11000	2.00868	0.51000	651.82	73.98	5.36
4-(2-Ethoxy)ethoxy- β -nitrostyrene	2.2010	19.7500	0.977475	-0.12000	2.00795	0.61000	836.76	77.58	6.14

*1,4-Dioxane used as solvent; benzene used as solvent on all others

b. Capacitance bridge.--The capacitance bridge was General Radio Company Type 716-C, operated by the substitutional method, at a frequency (f_0) of 10 kc. and a factor (M) of 1.

c. Oscillator.--The oscillator was General Radio Company Type 1302-A, operated at a frequency of 10 kc.

d. Substitutional capacitor.--This was General Radio Company Type 722-N, using 400 micromicrofarads as the zero base.

B. Ultra-violet Absorption Spectra.--The ultra-violet absorption spectrum of each compound was obtained for various concentrations of the compound in absolute ethanol solution. A Bausch and Lomb Spectronic 505 double-beam recording spectrophotometer was used with a matched pair of 1.000 cm. quartz cells, using a matched set of 9.90 mm. quartz spacers. The absorbance values for the various solutions were corrected for solvent absorbance, by recording solvent against solvent on the same paper used for the spectra of the compound used as solute, and subtracting these values from the observed absorbance values. These corrected absorbance values were then plotted against the concentration of the solutions, thus giving a check of the applicability of Beer's law. Only values which showed good or better applicability of Beer's law were used in the determination of the extinction coefficient. The results of these studies are briefly summarized in Table 2, and are given in detail in Figures 1-10.

C. Infrared Absorption Spectra.--The infrared absorption spectrum of each compound was obtained using (a) plates or thin

TABLE 2

TABULATION OF MAXIMA IN ULTRA-VIOLET ABSORPTION SPECTRA

Compound	Alkyloxy Substituent			
	Vinylloxy		Ethoxy	
	λ_{\max} (m μ)	$\log_{10} \epsilon$	λ_{\max} (m μ)	$\log_{10} \epsilon$
2- <u>Alkyloxy</u> ethoxy- benzene	218.5	3.92	195.0	4.53
	265.0	3.11	220.5	3.94
	270.0	3.24	271.0	3.26
	276.5	3.17	277.5	3.18
2-(2- <u>Alkyloxy</u>)ethoxy- benzaldehyde	213.0	4.27	214.0	4.36
	252.0	3.95	251.0	4.06
	317.0	3.60	318.0	3.71
3-(2- <u>Alkyloxy</u>)ethoxy- benzaldehyde	217.0	4.36	218.5	4.41
	251.0	3.92	251.5	4.00
	310.0	3.44	310.0	3.50
4-(2- <u>Alkyloxy</u>)ethoxy- benzaldehyde	205.5	4.09	197.0	4.24
	218.0	4.14	219.0	4.15
	274.5	4.26	275.0	4.30
2-(2- <u>Alkyloxy</u>)ethoxy- styrene	207.0	4.44	210.0	4.40
	247.5	4.10	246.0	4.12
	299.0	3.59	300.0	3.65
3-(2- <u>Alkyloxy</u>)ethoxy- styrene	214.0	4.47
	249.0	4.06
	294.0	3.36
4-(2- <u>Alkyloxy</u>)ethoxy- styrene	208.0	4.24	205.0	4.34
	261.5	4.18	258.5	4.37
	280.0	3.89	290.0	3.49
	288.0	3.80	303.0	3.23
2-(2- <u>Alkyloxy</u>)ethoxy- β -nitrostyrene	199.0	4.50	201.0	4.45
	240.0	3.92	242.5	3.97
	300.0	4.03	302.5	4.08
	346.0	4.03	350.0	4.03
3-(2- <u>Alkyloxy</u>)ethoxy- β -nitrostyrene	202.5	4.39
	222.0	3.94
	248.0	3.88
	307.0	4.19
4-(2- <u>Alkyloxy</u>)ethoxy- β -nitrostyrene	195.5	4.53	197.0	4.37
	236.0	4.02	239.0	4.01
	346.0	4.32	350.0	4.32

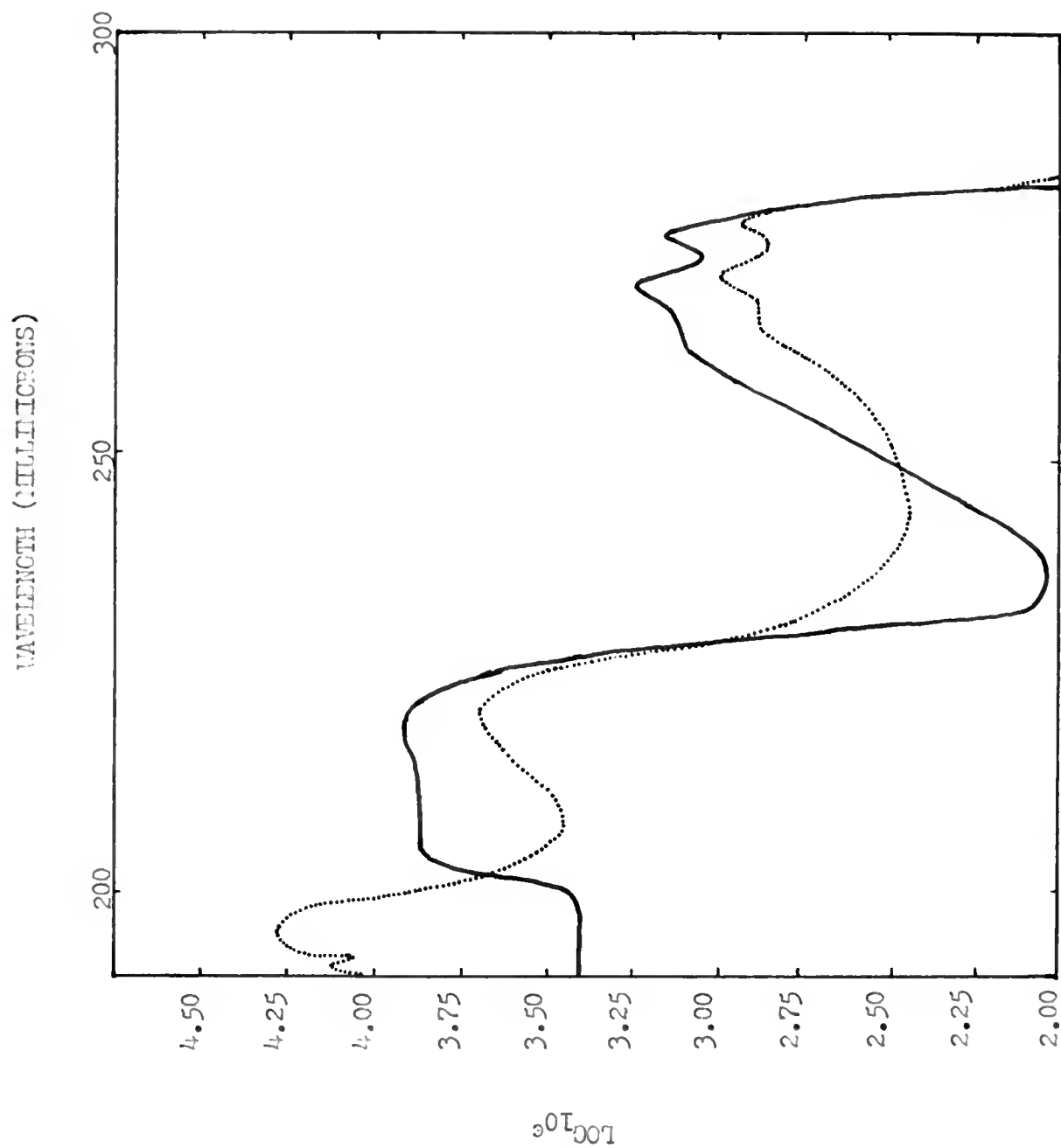


Figure 1.---ULTRA-VIOLET ABSORPTION SPECTRA OF 2-VINYLOXYTHIOBENZENE (SOLID CURVE) AND 2-ETHYLOXYTHIOBENZENE (DOTTED CURVE)

WAVELENGTH (MILLIMICRONS)

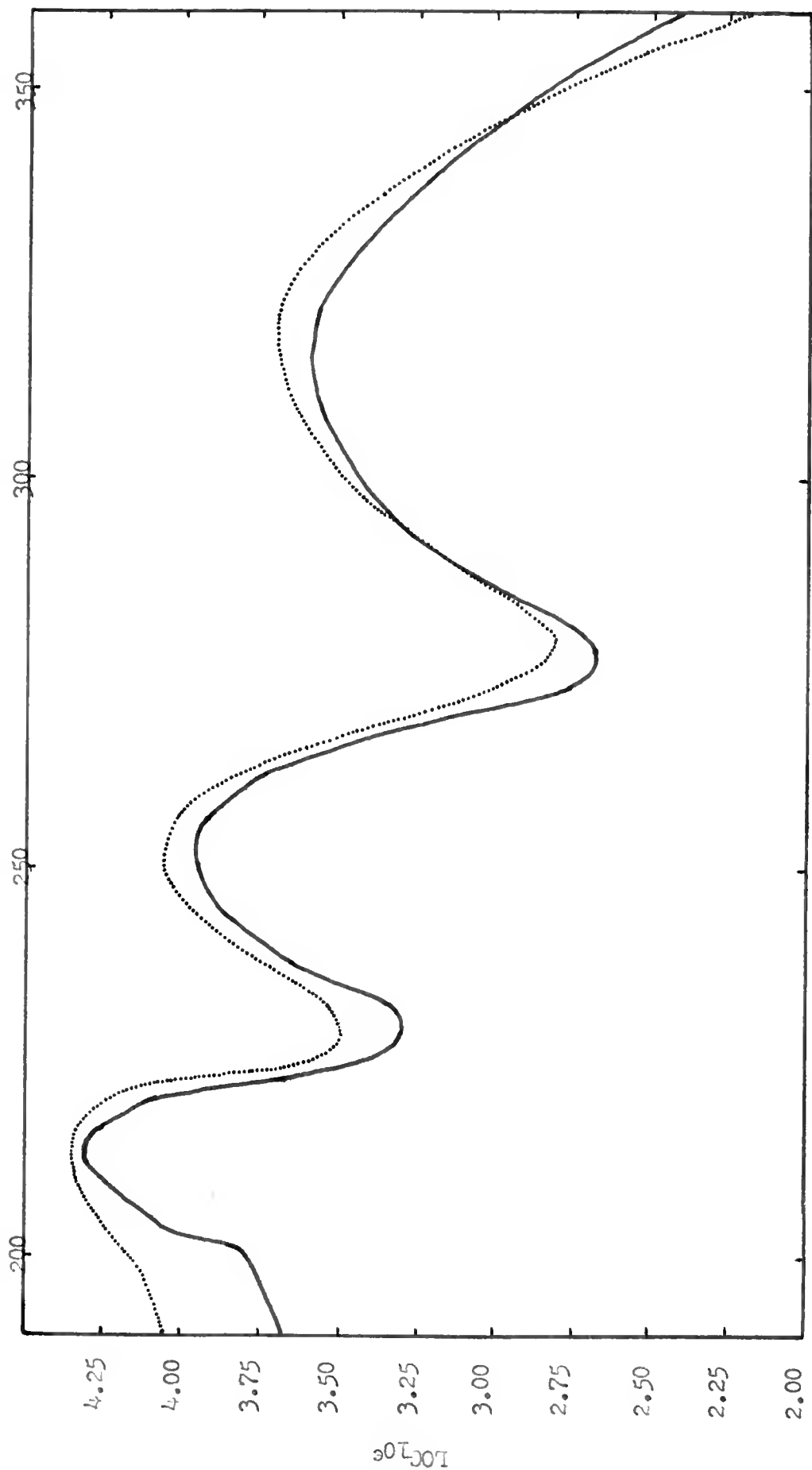


Figure 2.---ULTRA-VIOLET ABSORPTION SPECTRA OF 2-(2-VINYLOXY)ETHOXYBENZALDEHYDE (SOLID CURVE) AND 2-(2-ETHYLOXY)ETHOXYBENZALDEHYDE (DOTTED CURVE).



Figure 3.---ULTRAVIOLET ABSORPTION SPECTRA OF 3-(2-VINYLOXY)ETHOXYBENZALDEHYDE (SOLID CURVE)
AND 3-(2-ETHYLOXY)ETHOXYBENZALDEHYDE (DOTTED CURVE).

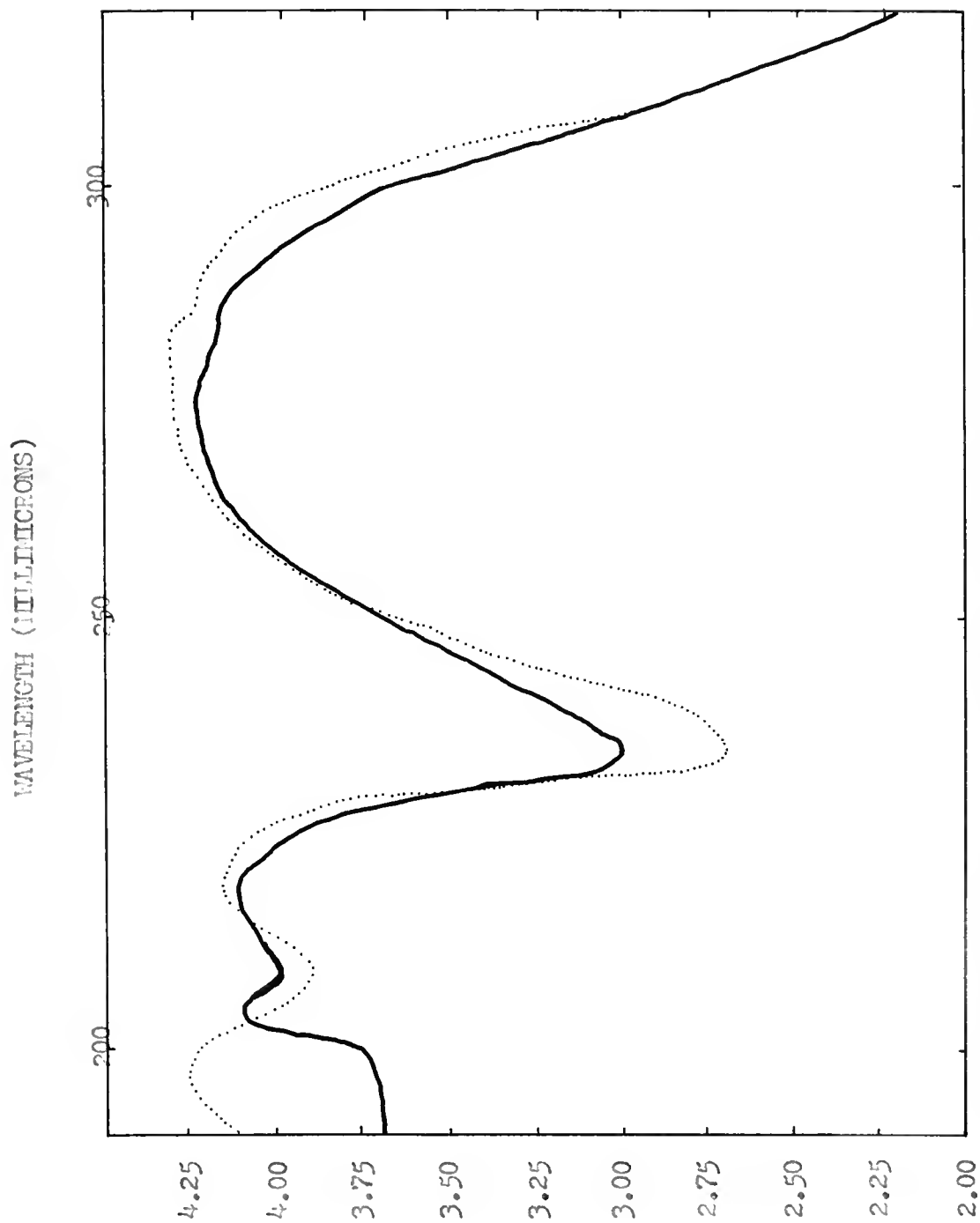


Figure 4.---ULTRA-VIOLET ABSORPTION SPECTRA OF 4-(2-VINYLOXY)ETHOXYBENZALDEHYDE (SOLID CURVE) AND 4-(2-ETHYLOXY)ETHOXYBENZALDEHYDE (DOTTED CURVE).

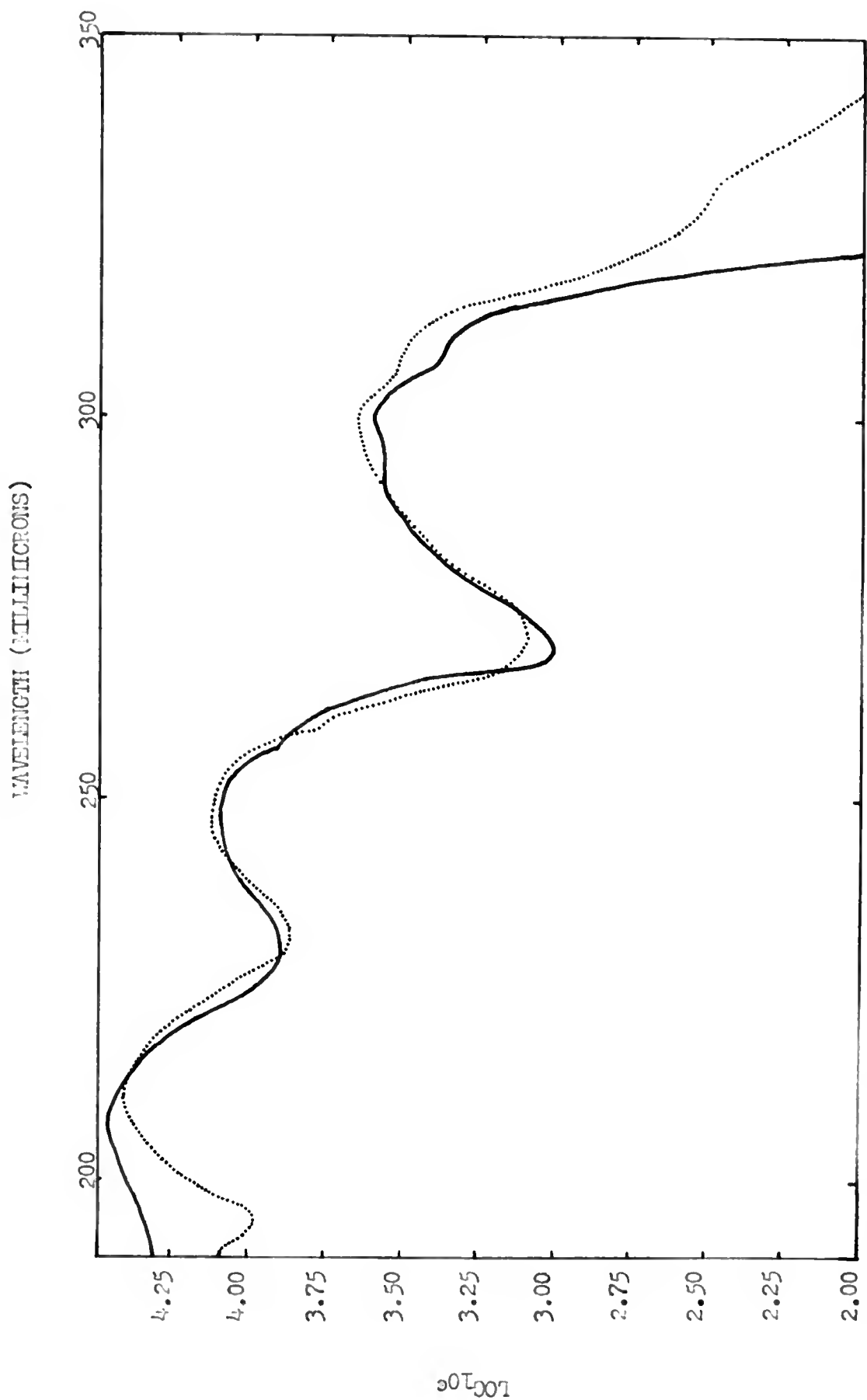


Figure 5.---ULTRA-VIOLET ABSORPTION SPECTRA OF 2-(2-VINLOXY)ETHOXYSTYRENE (SOLID CURVE) AND 2-(2-ETHYLOXY)ETHOXYSTYRENE (DOTTED CURVE).

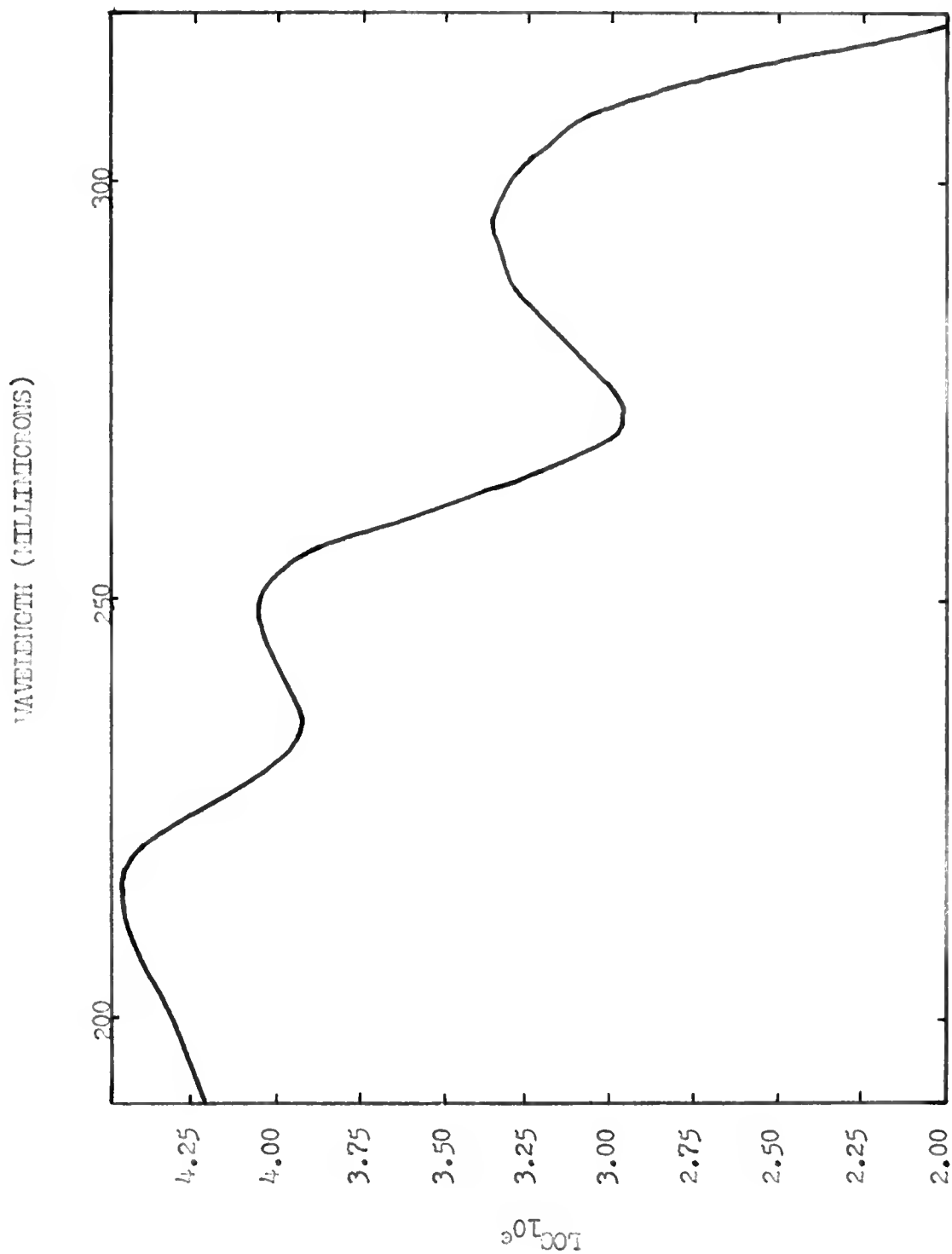


Figure 6.--ULTRA-VIOLET ABSORPTION SPECTRUM OF 3-(2-VINYLOXY)ETHOXYSTYRENE.

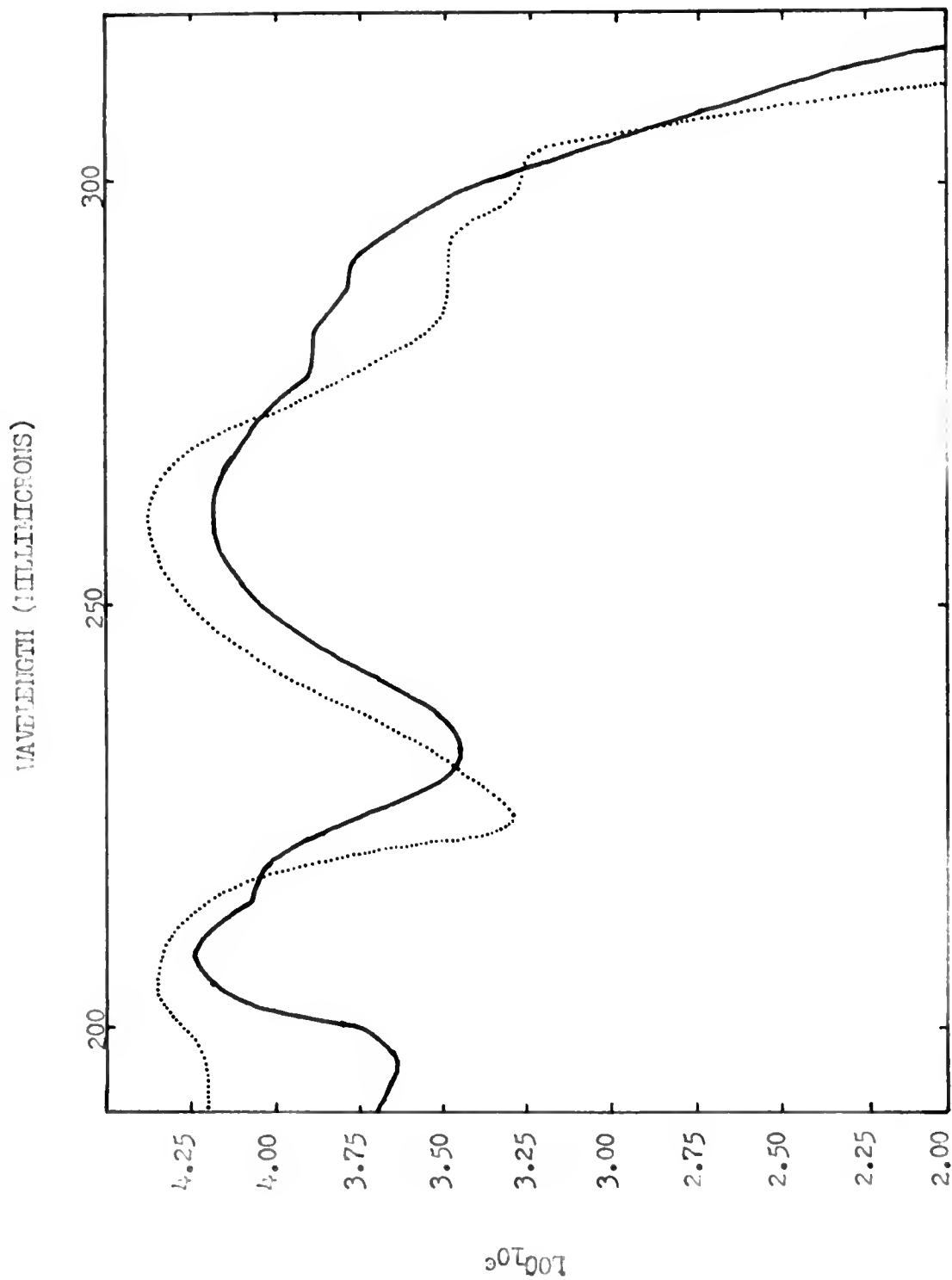


Figure 7.---ULTRA-VIOLET ABSORPTION SPECTRA OF 4--(2-VINYLOXY)ETHOXYSTYRENE (SOLID CURVE) AND 4--(2-ETHYLOXY)ETHOXYSTYRENE (DOTTED LINE).

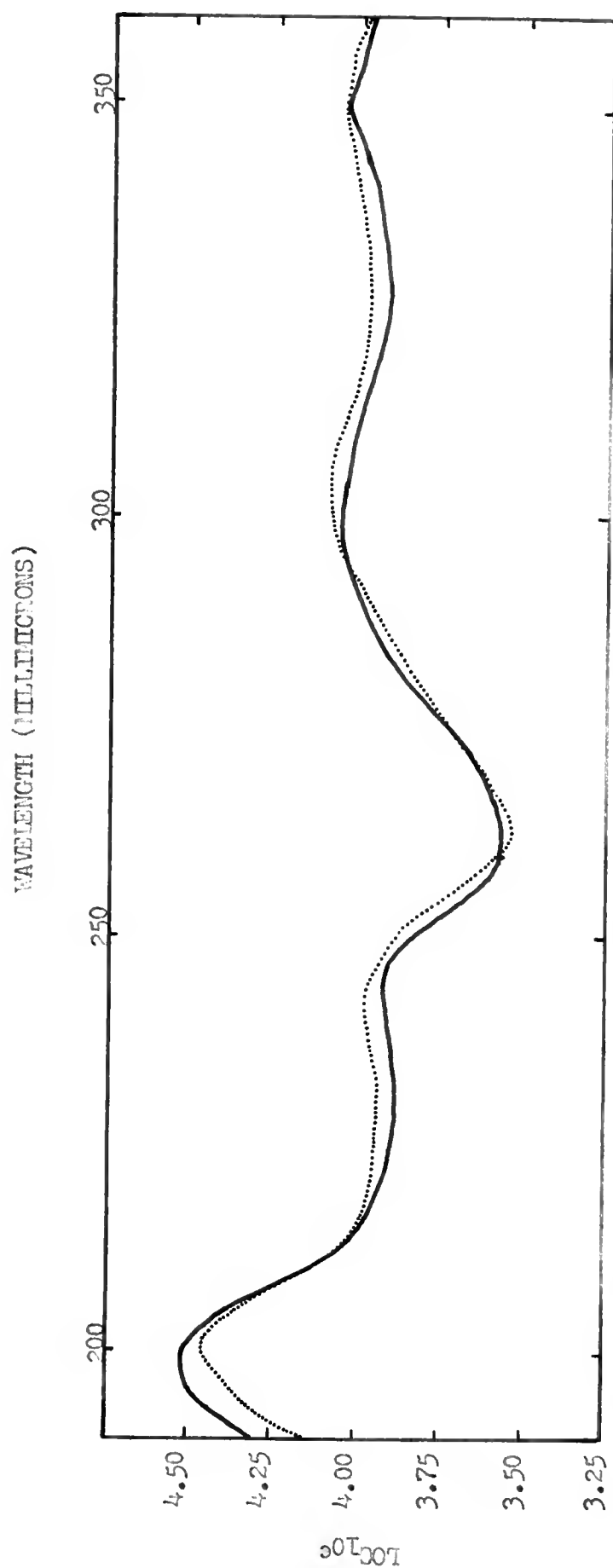


Figure 8.---ULTRA-VIOLET ABSORPTION SPECTRA OF 2-(2-VINLOXY)ETHOXY-β-NITROSTYRENE (SOLID CURVE)
AND 2-(2-ETHNLOXY)ETHOXY-β-NITROSTYRENE (DOTTED CURVE).

WAVELENGTH (MILLICONS)

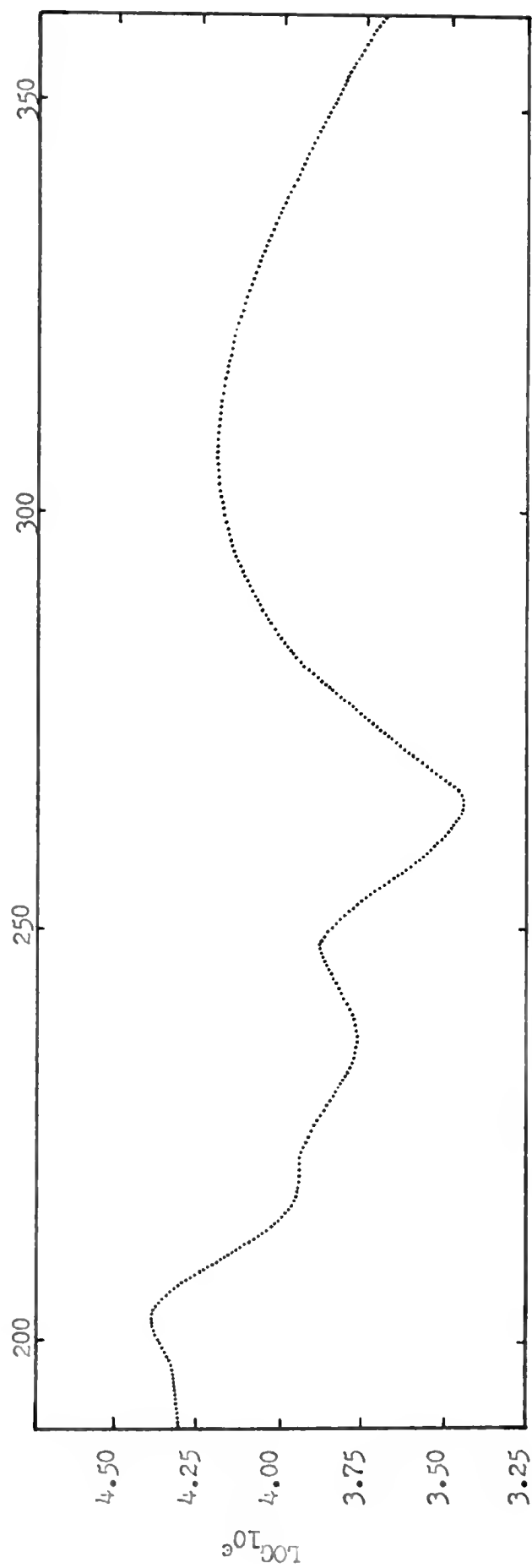


Figure 9. ---ULTRA-VIOLET SPECTRUM OF 3-(2-ETHOXY)ETHOXY- β -NITROSTYRENE.

WAVELENGTH (MILLIMICRONS)

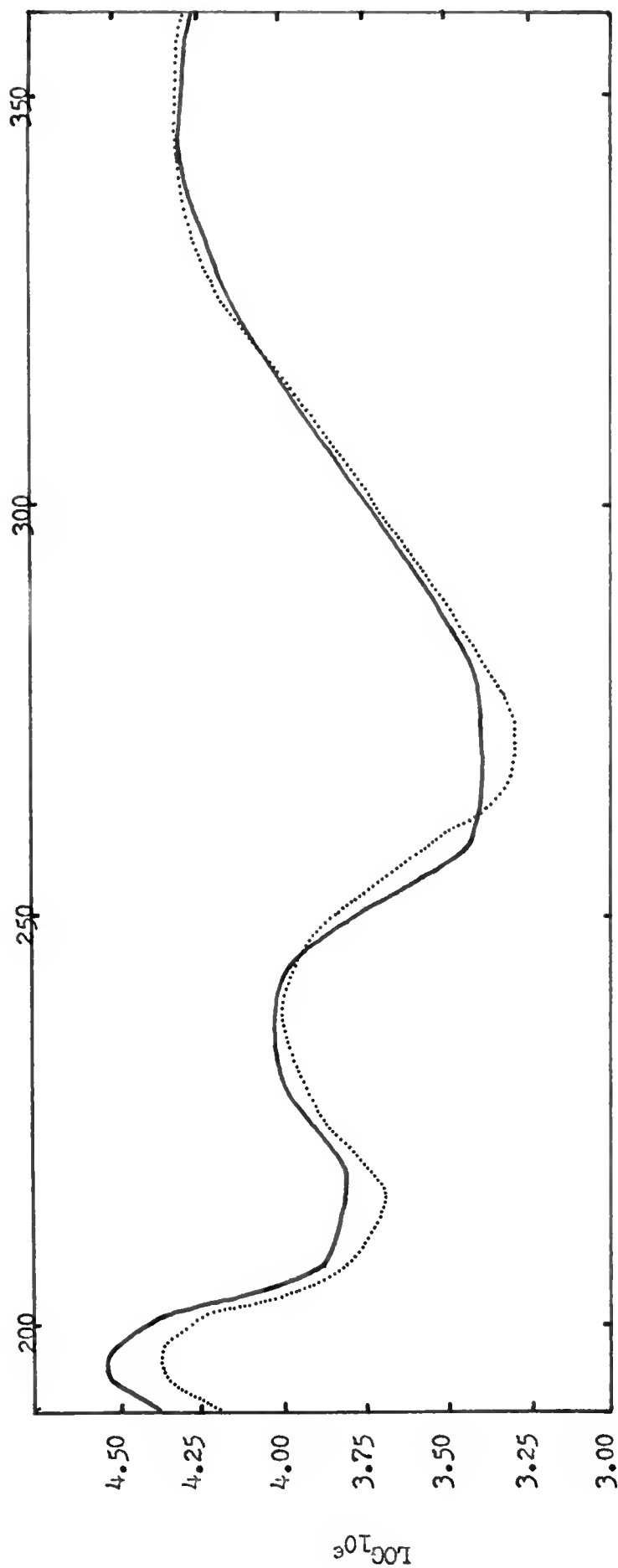


Figure 10.---ULTRA-VIOLET ABSORPTION SPECTRA OF 4-(2-VINYLOXY)ETHOXY-β-NITROSTYRENE (SOLID CURVE) AND 4-(2-ETHYLOXY)ETHOXY-β-NITROSTYRENE (DOTTED CURVE).

cells with the neat liquid, in the case of liquid compounds, and (b) carbon tetrachloride solution, Nujol or a similar oil mull, potassium bromide pellet, or liquid melt, as appropriate, for solid compounds. Both sodium chloride and calcium fluoride prisms were used. Using all of these variables, the spectrum of each compound reported represented the best of the obtained spectra. A Perkin-Elmer Corporation Model 21 double-beam recording spectrophotometer was used for all spectra. In the following description of the spectra, the following order is used: frequency, in wavenumbers (cm^{-1}), relative intensity of the peak (strong, s.; medium, m.; and weak, w.), its shape (sharp, s.; moderate, m.; and broad, b.), and the assignment of the peak.

1. 2-Vinyloxyethoxybenzene.--3125 w., m., C-H stretch of the alpha hydrogen of vinyloxy group; 3067, m., b., asymmetric C-H stretch of beta hydrogens of vinyloxy group; 3049, m., s., symmetric C-H stretch of beta hydrogens of vinyloxy group; 2924, s., s., asymmetric C-H stretch in ethylene group; 2882, s., s., symmetric C-H stretch in ethylene group; 1639, 1621. s., s., C-C stretch in vinyloxy group; 1600, 1587, 1495, all s., s., C-C stretch in phenyl group; 1435, s., s., C-H bend in ethylene group; 1366, m., s., C-C stretch in ethylene group; 1321, s., s., asymmetric C-C stretch in vinyloxy group; 1302, 1294, m., s., symmetric C-C stretch in vinyloxy group; 1245, s., s., phenyl C-O stretch in phenyl ether; 1199, s., s., vinyl C-O stretch in vinyloxy group; 1175, m., s., aliphatic C-O stretch in ethoxy group.

2. 2-(2-Vinyloxy)ethoxybenzaldehyde.--3067, w., m., C-H stretch of beta hydrogens in vinyloxy group; 2924, w., s., asymmetric C-H stretch in ethylene group; 2874, w., s., symmetric C-H stretch in ethylene group; 1689, s., s., C-O stretch in aldehyde group; 1639, 1621, m., s., C-C stretch in vinyloxy group; 1600, 1484, s., s., C-C stretch in phenyl group; 1453, m., s., C-H bend in ethylene group; 1397. m., s., C-C stretch in phenyl-aldehyde group; 1366, s., s., C-C stretch in ethylene group; 1322, s., s., asymmetric C-C stretch in vinyloxy group; 1289, s., s., symmetric C-C stretch in vinyloxy group; 1244, s., s., phenyl C-O stretch in phenyl ether; 1198, s., s., vinyl C-O stretch in vinyloxy group; 1155, m., s., aliphatic C-O stretch in ethoxy group.

3. 3-(2-Vinyloxy)ethoxybenzaldehyde.--3067, w., s., asymmetric C-H stretch of beta hydrogens in vinyloxy group; 2941, m., s., symmetric C-H stretch of beta hydrogens in vinyloxy group; 2882, w., s., asymmetric C-H stretch in ethylene group; 2849, w., s., symmetric C-H stretch in ethylene group; 2825, 2740, w., s., C-H stretch in aldehyde group; 1695, s., s., C-O stretch in aldehyde group; 1639, 1621, m., m., C-C stretch in vinyloxy group; 1597, 1585, 1484, s., s., C-C stretch in phenyl group; 1449 s., s., C-H bend in ethylene group; 1389, m., s., C-C stretch in phenyl-aldehyde group; 1362, w., s., C-C stretch in ethylene group; 1323, s., s., asymmetric C-C stretch in vinyloxy group; 1282, s., s., symmetric C-C stretch in vinyloxy group; 1264, s., m., phenyl C-O stretch in phenyl

ether; 1199, s., s., vinyl C-O stretch in vinyloxy group;
1164, m., s., aliphatic C-O stretch in ethoxy group.

4. 4-(2-Vinyloxy)ethoxybenzaldehyde.-- 3125, w., s.,
C-H stretch of alpha hydrogen in vinyloxy group; 3077, w., s.,
asymmetric C-H stretch of beta hydrogens in vinyloxy group;
2941, w., m., symmetric C-H stretch of beta hydrogens in vinyloxy
group; 2882, w., m., asymmetric C-H stretch in ethylene group;
2874, w., s., symmetric C-H stretch in ethylene group; 2817,
2732, w., s., C-H stretch in aldehyde group; 1704, s., s.,
C-O stretch in aldehyde group; 1639, 1618, s., s., C-C stretch
in vinyloxy group; 1603, 1582, 1508, 1481, m., s., C-C stretch
in phenyl group; 1453, w., s., C-H bend in ethylene group;
1429, w., s., para-substituted benzene; 1389, w., s., C-C
stretch in phenyl-aldehyde group; 1368, w., s., C-C stretch in
ethylene group; 1324, m., s., asymmetric C-C stretch in vinyloxy
group; 1261, s., s., symmetric C-C stretch in vinyloxy group;
1230, w., s., phenyl C-O stretch in phenyl ether; 1202, s., s.,
vinyl C-O stretch in vinyloxy group; 1163, m., m., aliphatic
C-O stretch in ethoxy group.

5. 2-(2-Vinyloxy)ethoxystyrene.--3067, m., m., asymmetric
C-H stretch of beta hydrogens in vinyloxy group; 3030, m., m.,
symmetric C-H stretch of beta hydrogens in vinyloxy group; 2924,
s., s., asymmetric C-H stretch in ethylene group; 2874, s., s.,
symmetric C-H stretch in ethylene group; 1639, 1618, m., m.,
C-C stretch in vinyloxy group; 1597, 1577, 1484, s., s., C-C
stretch in phenyl group; 1449, s., s., C-H bend in ethylene group;

1412, m., s., C-H stretch in vinyl of styrene group; 1366, m., s., C-C stretch in ethylene group; 1322, s., s., asymmetric C-C stretch in vinyloxy group; 1290, s., s., asymmetric C-C stretch in vinyloxy group; 1241, s., m., phenyl C-C stretch in phenyl ether; 1199, s., s., vinyl C-O stretch in vinyloxy group; 1133, m., m., aliphatic C-O stretch in ethoxy group.

6. 3-(2-Vinyloxy)ethoxystyrene.--3125, w., s., C-H stretch of alpha hydrogen in vinyloxy group; 3077, m., s., asymmetric C-H stretch of beta hydrogens in vinyloxy group; 2933, s., s., symmetric C-H stretch of beta hydrogens in vinyloxy group; 2874, w., m., asymmetric C-H stretch in ethylene group; 2817, w., m., symmetric C-H stretch in ethylene group; 1637, 1617, s., s., C-C stretch in vinyloxy group; 1605, 1597, 1582, 1575, 1511, 1484, all s. to m., s., C-C stretch in phenyl group; 1445, s., s., C-H bend in ethylene group; 1414, w., m., C-H stretch in vinyl of styrene group; 1366, w., m., C-C stretch in ethylene group; 1323, s., s., asymmetric C-C stretch in vinyloxy group; 1287, s., s., symmetric C-C stretch in vinyloxy group; 1264, 1244, s., s., phenyl C-O stretch in phenyl ether; 1199, s., s., vinyl C-O stretch in vinyloxy group; 1172, m., m., aliphatic C-O stretch in ethoxy group.

7. 4-(2-Vinyloxy)ethoxystyrene.--3058, w., s., asymmetric C-H stretch of beta hydrogens in vinyloxy group; 2924, w., s., symmetric C-H stretch of beta hydrogens in vinyloxy group; 1639, 1618, m., s., C-C stretch in vinyloxy group; 1605, 1577, 1511, w., m., C-C stretch in phenyl group; 1451, m., s., C-H bend in

ethylene group; 1410, m., m., stretch in vinyl of styrene group; 1370, m., s., C-C stretch in ethylene group; 1325, s., s., asymmetric C-C stretch in vinyloxy group; 1285, s., s., symmetric C-C stretch in vinyloxy group; 1250, 1241, s., s., phenyl C-O stretch in phenyl ether; 1202, s., s., vinyl C-O stretch in vinyloxy group; 1163, m., m., aliphatic C-O stretch in ethoxy group.

8. 2-(2-Vinyloxy)ethoxy- β -nitrostyrene.--3125, w., m., C-H stretch of alpha hydrogen in vinyloxy group; 3077, w., m., asymmetric C-H stretch of beta hydrogens in vinyloxy group; 2985, m., s., symmetric C-H stretch of beta hydrogens in vinyloxy group; 2924, s., s., asymmetric C-H stretch in ethylene group; 2865, w., m., symmetric C-H stretch in ethylene group; 1631, 1605, s., s., C-C stretch in vinyloxy group; 1575, 1506, 1493, s., s., C-C stretch in phenyl group; 1449, m., s., C-H bend in ethylene group; 1366, s., s., C-C stretch in ethylene group; 1321, m., s., asymmetric C-C stretch in vinyloxy group; 1299, w., s., symmetric C-C stretch in vinyloxy group; 1250, m., s., phenyl C-O stretch in phenyl ether; 1198, s., s., vinyl C-O stretch in vinyloxy group; 1161, m., s., aliphatic C-O stretch in ethoxy group.

9. 4-(2-Vinyloxy)ethoxy- β -nitrostyrene.--3106, m., m., asymmetric C-H stretch of beta hydrogens in vinyloxy group; 2924, m., m., symmetric C-H stretch of beta hydrogens in vinyloxy group; 2899, s., m., asymmetric C-H stretch in ethylene group; 2857, s., m., symmetric C-H stretch in ethylene group; 1621, m., s., C-C stretch in vinyloxy group; 1600, 1570, 1508, 1490,

m., s., C-C stretch in phenyl group; 1451, s., s., C-H bend in ethylene group; 1425, m., m., para-substituted benzene; 1374, s., s., C-C stretch in ethylene group; 1332, m., m., asymmetric C-C stretch in vinyloxy group; 1307, s., s., symmetric C-C stretch in vinyloxy group; 1248, s., s., phenyl C-O stretch in phenyl C-O stretch in phenyl ether; 1193, s., s., vinyl C-O stretch in vinyloxy group; 1171, s., m., aliphatic C-O stretch in ethoxy group.

10. 2-Ethoxyethoxybenzene.--3067, w., m., asymmetric C-H stretch in ethyloxy group; 2985, m., s., symmetrical C-H stretch in ethyloxy group; 2924, m., s., asymmetric C-H stretch in ethoxy group; 2874, m., s., symmetrical C-H stretch in ethoxy group; 1603, s., s., C-C stretch in phenyl group; 1590, s., s., C-C stretch in phenyl group; 1497, s., s., C-H deformation in CH₂ units; 1453, m., s., asymmetrical CH₃ deformation in ethyloxy group; 1389, w., m., C-C stretch in phenyl group; 1374, m., s., symmetrical CH₃ deformation in ethyloxy group; 1355, m., s., (unassigned); 1333, w., b., C-C stretch in phenyl group; 1304, m., m., C-C stretch in phenyl group; 1292, 1274, phenyl C-O stretch in phenyl ether; 1174, m., s., aliphatic C-O stretch in ethoxy and ethyloxy groups.

11. 2-(2-Ethoxy)ethoxybenzaldehyde.--3067, w., m., asymmetrical C-H stretch in ethyloxy group; 2976, m., s., symmetrical C-H stretch in ethyloxy group; 2924, m., s., asymmetrical C-H stretch in ethoxy group; 2865, m., s., symmetrical C-H stretch in ethoxy group; 2762, w., m., C-H stretch in aldehyde group; 1689, s., s., C=O stretch in aldehyde group; 1597, 1582,

s., s., C-C stretch in phenyl group; 1484, s., s., C-H deformation in CH_2 units; 1458, s., m., asymmetrical CH_3 deformation in ethyloxy group; 1397, m., s., C-C stretch in phenyl group; 1372, m., m., symmetrical CH_3 deformation in ethyloxy group; 1353, w., m., (unassigned); 1302, w., m., C-C stretch in phenyl group; 1287, 1244, s., m., phenyl-C-O stretch in phenyl ether; 1189, s., m., bending the ortho-disubstituted benzene; 1163, s., s., aliphatic C-O stretch in ethyloxy and ethoxy groups.

12. 3-(2-Ethyloxy)ethoxybenzaldehyde.--3067, w., m., asymmetrical C-H stretch in ethyloxy group; 2985, m., s., symmetrical C-H stretch in ethyloxy group; 2933, m., s., asymmetrical C-H stretch in ethoxy group; 2874, m., m., symmetrical C-H stretch in ethoxy group; 2740, w., m., C-H stretch in aldehyde group; 1704, 1701, s., s., C-O stretch in aldehyde group; 1597, 1585, s., s., C-C stretch in phenyl group; 1484, s., s., C-H deformation in CH_2 units; 1449, s., m., asymmetrical CH_3 deformation in ethyloxy group; 1389, m., m., C-C stretch in phenyl group; 1376, m., m., symmetrical CH_3 deformation in ethyloxy group; 1355, w., m., (unassigned); 1325, m., m., C-C stretch in phenyl group; 1290, 1266, s., m., phenyl-C-O stretch in phenyl ether; 1171, m., m., aliphatic C-O stretch in ethoxy and ethyloxy groups.

13. 4-(2-Ethyloxy)ethoxybenzaldehyde.--3067, w., m., asymmetrical C-H stretch in ethyloxy group; 2976, m., s., symmetrical C-H stretch in ethyloxy group; 2933, m., s., asymmetrical C-H stretch in ethoxy group; 2874, m., s., symmetrical C-H stretch in ethoxy group; 2740, m., m., C-H stretch in aldehyde group; 1692, 1686, s., s., C-O stretch in aldehyde group; 1603, 1577, s., s.,

C-C stretch in phenyl group; 1508, s., s., C-H deformation in CH₂ units; 1451, m., m., asymmetrical CH₃ deformation in ethyloxy group; 1422, m., m., para-disubstituted benzene; 1393, w., m., C-C stretch in phenyl group; 1374, w., m., symmetrical CH₃ deformation in ethyloxy group; 1355, w., m., (unassigned); 1312, m., s., C-C stretch in phenyl group; 1261, 1235, 1217, s., m., phenyl-C-O stretch in phenyl ether; 1163, s., s., aliphatic C-O stretch in ethoxy and ethyloxy groups.

14. 2-(2-Ethyloxy)ethoxystyrene.--3067, w., m., asymmetrical C-H stretch in ethyloxy group; 3021, w., m., C-H stretch of alpha hydrogens in styrene group; 2976, m., s., symmetrical C-H stretch in ethyloxy group; 2933, m., s., asymmetrical C-H stretch in ethoxy group; 2874, m., s., symmetrical C-H stretch in ethoxy group; 1629, s., s., C-C stretch in vinyl of styrene group; 1603, 1577, s., s., C-C stretch in phenyl group; 1486, s., s., C-H deformation in CH₂ units; 1451, s., s., asymmetrical CH₃ deformation in ethyloxy group; 1418, m., m., CH₂ deformation in vinyl of styrene group; 1385, w., m., C-C stretch in phenyl group; 1374, m., m., symmetrical CH₃ deformation in ethyloxy group; 1355, w., m. (unassigned); 1316, m., m., C-C stretch in phenyl group; 1294, s., m., C-H deformation of alpha hydrogen in vinyl of styrene group; 1247, s., m., phenyl-C-O stretch in phenyl ether; 1190, w., m., bending in ortho-disubstituted benzene; 1163, m., m., aliphatic C-O stretch in ethyloxy and ethoxy groups.

15. 4-(2-Ethyloxy)ethoxystyrene.--3096, w., m., asymmetric C-H stretch in ethyloxy group; 3049, w., m., C-H

stretch of alpha hydrogens in styrene group; 2994, m., s., symmetric C-H stretch in ethyloxy group; 2941, m., s., asymmetrical C-H stretch in ethoxy group; 2882, m., s., symmetrical C-H stretch in ethoxy group; 1631, m., m., C-C stretch in vinyl of styrene group; 1610, s., s., C-C stretch in phenyl group; 1577, w., m., C-C stretch in phenyl group; 1511, s., s., C-H deformation in CH_2 units; 1456, w., s., asymmetrical CH_3 deformation in ethyloxy group; 1422, w., m., para-disubstituted benzene; 1412, w., m., CH_2 deformation in vinyl of styrene group; 1385, w., m., C-C stretch in phenyl group; 1374, w., s., symmetrical CH_3 deformation in ethyloxy group; 1355, w., m. (unassigned); 1304, w., m., C-C stretch in phenyl group; 1294, C-H deformation of alpha hydrogen in vinyl of styrene group; 1238, s., s., phenyl-C-O stretch in phenyl ether; 1178, s., s., aliphatic C-O stretch in ethyloxy and ethoxy groups.

16. 2-(Ethyloxy)ethoxy- β -nitrostyrene.--3115, w., s., C-H stretch in vinyl of beta-nitrostyrene group; 3086, w., m., asymmetrical C-H stretch in ethyloxy group; 2994, m., s., symmetrical C-H stretch in ethyloxy group; 2941, m., s., asymmetrical C-H stretch in ethoxy group; 2890, m., s., symmetrical C-H stretch in ethoxy group; 1637, s., s., C-C stretch of vinyl in beta-nitrostyrene group; 1605, 1580, s., s., C-C stretch in phenyl group; 1550, m., b., C-N stretch in beta-nitrostyrene group; 1524, 1520, 1515, s., s., C-Cl stretch in CCl_4 (solvent); 1495, m., s., C-H deformation in CH_2 units; 1451, s., s., asymmetrical CH_3 deformation in ethyloxy group; 1389, w., m., C-C stretch in phenyl group; 1377, w., m., symmetrical CH_3

deformation in ethyloxy group; 1344, s., m., C-N stretch in beta-nitrostyrene; 1304, m., m., C-C stretch in phenyl group; 1294, m., m., C-H deformation of alpha hydrogen in vinyl of beta-nitrostyrene; 1258, s., s., phenyl-C-O stretch in phenyl ether; 1196, m., m., bending in ortho-disubstituted benzene; 1166, m., m., aliphatic C-O stretch in ethoxy and ethyloxy groups.

17. 3-(2-Ethyloxy)ethoxy-β-nitrostyrene.--3125, w., s., C-H stretch in vinyl of beta-nitrostyrene group; 3077, w., m., asymmetrical C-H stretch in ethyloxy group; 2994, m., s., symmetrical C-H stretch in ethyloxy group; 2941, m., s., asymmetrical C-H stretch in ethoxy group; 2882, m., s., symmetrical C-H stretch in ethoxy group; 1642, s., s., C-C stretch in vinyl of beta-nitrostyrene group; 1603, 1580, m., m., C-C stretch in phenyl group; 1563, 1550, w., m., C-N stretch in beta-nitrostyrene; 1527, s., s., C-Cl stretch in CCl₄ (solvent); 1486, m., m., C-H deformation in CH₂ units; 1445, m., m., asymmetrical CH₃ deformation in ethyloxy group; 1391, w., m., C-C stretch in phenyl group; 1376, w., m., symmetrical CH₃ deformation in ethyloxy group; 1348, s., s., C-N stretch in beta-nitrostyrene; 1318, w., m., C-C stretch in phenyl group; 1299, m., s., C-H deformation of alpha hydrogen in vinyl of beta-nitrostyrene; 1274, s., s., phenyl-C-O stretch in phenyl ether; 1232, m., m., C-Cl stretch in CCl₄ (solvent); 1178, m., m., aliphatic C-O stretch in ethoxy and ethyloxy groups.

18. 4-(2-Ethyloxy)ethoxy-β-nitrostyrene.--3115, w., m., C-H stretch in vinyl of beta-nitrostyrene group; 3040, w., m.,

asymmetrical C-H stretch in ethyloxy group; 2976, m., s.,
 symmetrical C-H stretch in ethyloxy group; 2924, m., s.,
 asymmetrical C-H stretch in ethoxy group; 2874, m., s.,
 symmetrical C-H stretch in ethoxy group; 1634, s., s., C-C
 stretch in vinyl of beta-nitrostyrene group: 1605, 1572, s., s.,
 C-C stretch in phenyl group; 1546. m., b., C-N stretch in
 beta-nitrostyrene; 1522, s., s., C-Cl stretch in CCl_4 (solvent);
 1508, C-H deformation in CH_2 units; 1453, m., s., asymmetrical
 CH_3 deformation in ethyloxy group; 1425, m., s., para-disubstituted
 benzene; 1385, w., m., C-C stretch in phenyl group; 1374, w., m.,
 symmetrical CH_3 deformation in ethyloxy group; 1350, s., s.,
 C-N stretch in beta-nitrostyrene; 1309, m., s., C-C stretch in
 phenyl group; 1294, w., s., C-H deformation of alpha hydrogen
 in vinyl of beta-nitrostyrene; 1255, s., m., phenyl-C-O stretch
 in phenyl ether; 1238, m., m., C-Cl stretch in CCl_4 (solvent);
 1174, s., s., aliphatic C-O stretch in ethoxy and ethyloxy
 groups.

D. Molar Refraction and Exaltation of Molar Refraction.--The
 values for the experimentally determined molar refractions were
 a by-product in the dipole moment determination. As such, both
 for solids and liquids, all of the experimental determinations
 were made at the same temperature, 30.0°C. The calculations
 were executed according to the methods of Vogel (17) and
 Eisenlohr (18). The values of the atomic and group parameters
 used in these calculations were as follows:

Quantity	Value of Parameter	
	Vogel	Eisenlohr
Carbon atom	2.591	2.418
Hydrogen atom	1.028	1.100
Oxygen atom (carbonyl)	2.211	2.211
Oxygen atom (other)	1.764	1.643
Carbon-carbon double bond	1.575	1.733
Nitro group (aromatic)	7.30	7.30

The results of these determinations are tabulated in Tables 3 and 4.

TABLE 3

TABULATION OF MOLAR REFRACTION DATA
FOR VINYLOXY COMPOUNDS

Compound	Calculated		Found	Exaltation	
	Vogel	Eisenlohr		Vogel	Eisenlohr
2-Vinyloxyethoxy-benzene	48.07	47.60	48.33	0.26	0.73
2-(2-Vinyloxy)ethoxy-benzaldehyde	52.88	52.23	55.08	2.20	2.85
3-(2-Vinyloxy)ethoxy-benzaldehyde	52.88	52.23	54.26	1.38	2.03
4-(2-Vinyloxy)ethoxy-benzaldehyde	52.88	52.23	56.22	3.34	3.99
2-(2-Vinyloxy)ethoxy-styrene	56.89	56.37	59.14	2.25	2.77
3-(2-Vinyloxy)ethoxy-styrene	56.89	56.37	58.37	1.48	2.00
4-(2-Vinyloxy)ethoxy-styrene	56.89	56.37	58.66	1.77	2.29
2-(2-Vinyloxy)ethoxy- β -nitrostyrene	63.16	62.57	66.35	3.19	3.78
4-(2-Vinyloxy)ethoxy- β -nitrostyrene	63.16	62.57	71.40	8.24	8.83

TABLE 4

TABULATION OF MOLAR REFRACTION DATA
FOR ETHYLOXY COMPOUNDS

Compound	Calculated		Found	Exaltation	
	Vogel	Eisenlohr		Vogel	Eisenlohr
2-Ethyloxyethoxy- benzene	48.56	48.07	49.95	1.39	1.88
2-(2-Ethyloxy)ethoxy- benzaldehyde	53.36	52.69	54.99	1.63	2.30
3-(2-Ethyloxy)ethoxy- benzaldehyde	53.36	52.69	54.71	1.35	2.02
4-(2-Ethyloxy)ethoxy- benzaldehyde	53.36	52.69	55.97	2.61	3.28
2-(2-Ethyloxy)ethoxy- styrene	57.37	56.83	59.63	2.26	2.80
4-(2-Ethyloxy)ethoxy- styrene	57.37	56.83	60.34	2.97	3.51
2-(2-Ethyloxy)ethoxy- α -nitrostyrene	63.64	63.03	73.88	10.24	10.85
3-(2-Ethyloxy)ethoxy- β -nitrostyrene	63.64	63.03	73.98	10.34	10.95
4-(2-Ethyloxy)ethoxy- β -nitrostyrene	63.64	63.03	77.58	13.94	14.55

CHAPTER III

DISCUSSION OF RESULTS

Preparation of the Compounds

For the most part, the primary objectives of this investigation have been successfully realized. With the exception of 3-(2-vinyloxy)-ethoxy- β -nitrostyrene (which has not as yet been successfully prepared) and 3-(2-ethyloxy)ethoxystyrene (which was prepared, but not in a pure state), the nuclear magnetic resonance spectra, the infrared spectra, and the elemental analyses of the compounds were in agreement with the structures proposed. The yields of the various compounds, which will be discussed in more detail below, are quite respectable, and are the yields of the compounds in a state of high purity. Due to the relatively high boiling points of these compounds, no assay of their purity by the techniques of vapor phase chromatography was attempted.

A. Previously Prepared Compounds.--A comparison in the yields reported for those compounds prepared by the old "wet" method with the yields obtained for the same compounds prepared by the new "dry" method is presented in tabular form in Table 5, where the quantity "Per Cent Increase" has been calculated by the expression:

Per Cent Increase

$$= \frac{\text{per cent yield (new method)} - \text{per cent yield (old method)}}{\text{per cent yield (old method)}} \cdot 100.$$

TABLE 5
COMPARISON IN YIELDS
OF SYNTHETIC METHODS

Compound	Per Cent Yield		Per Cent Increase
	(Old Method)	(New Method)	
2-Vinyloxyethoxy- benzene	21.00	60.00	185.7
2-(2-Vinyloxy)ethoxy- benzaldehyde	31.53	73.95	134.6
3-(2-Vinyloxy)ethoxy- benzaldehyde	42.46	82.11 63.64*	93.38 ...*
4-(2-Vinyloxy)ethoxy- benzaldehyde	18.70	80.74**	331.8

* Solid modification, not previously reported, no comparison possible.

** This yield is of crystalline solid; the reported yeild from the old method was based on liquid, although it was reported that the liquid crystallized on standing.

The advantage of the new method seems quite apparent.

B. Styrenes.--The yields of these compounds are as follows: 2-(2-vinyloxy)ethoxystyrene: 36.34 per cent; 3-(2-vinyloxy)-ethoxystyrene: 31.80 per cent; 4-(2-vinyloxy)ethoxystyrene: 49.77 per cent; 2-(2-ethyloxy)ethoxystyrene: 32.69 per cent; and 4-(2-ethyloxy)ethoxystyrene: 42.59 per cent. These are not particularly high yields. There are probably two reasons for these comparatively low yields: first, it has been shown in this laboratory (19, 20) that the Wittig (14) reaction does not go to completion; and second, styrenes are known to undergo a facile thermal polymerization (21-27). A distillation, conducted at a temperature sufficiently elevated to allow separation of the styrene and the parent aldehyde, resulted in a large amount of polymeric residue in the distillation flask. The higher the temperature and pressure (the lower the vacuum), the more efficient the separation and the more polymeric residue. This fact, coupled with a close similarity in boiling points, is the main reason that 3-(2-ethyloxy)-ethoxystyrene was not prepared in a pure state. Various chromatographic techniques for the purification of this compound are under investigation at the present time.

C. Beta-Nitrostyrenes.--As far as the 2-vinyloxyethoxy- β -nitrostyrenes are concerned, the synthetic procedure used was extremely bad; that these compounds were formed at all is surprising, that they were isolated in as high yields as reported is even more so. The use of low temperature in the final stage

of this method undoubtedly diminished the rate of vinyl ether hydrolysis. The use of an inverted addition order (adding the neutralizing hydrochloric acid solution to the basic reaction mixture, so that there would be no excess of acid solution to catalyze the hydrolysis) was investigated. However, under these more ideal conditions, the desired compounds could not be isolated. For this practical reason the reported preparative methods, with their disadvantages, were used. In the 2-ethyloxyethoxy- β -nitrostyrenes, since there is little danger of a similar hydrolysis of the ethyl group, under the same reaction conditions, this method is satisfactory. The reason that the yields were no higher in these compounds is probably due to the reactivity of the polar beta-nitrostyrene group, especially towards polymerization. The mother liquors from the recrystallizations of these compounds always contained dark, viscous oils or gummy amorphous solids, indicating the presence of polymeric material.

Physical Measurements

In order to obtain a check on the accuracy of the method used to determine the dipole moments, the dipole moment of a rigorously purified sample of anisole was determined. The experimentally determined value of 1.25 D (in benzene at 30°C.) was in excellent agreement with the value of anisole quoted by Weissberger (28) of 1.25 D and in good agreement with Lumbroso's value (29) (in benzene at 20°C.) of 1.26 D. Thus

it was judged that this method is satisfactory for the desired degree of accuracy.

No definite quantitative conclusions can be drawn from these data until model compounds can be synthesized and their dipole moments determined in a systematic manner, so as to arrive at theoretical values for the dipole moments of these compounds. However, some qualitative comparisons with analogous compounds, the dipole moments of which are reported in the literature, can be made.

1. Benzene.--Lumbruso (29) determined the dipole moment of phenol (in benzene solution at 20°C.) to be 1.47 D and that of anisole (benzene, 20°C.) to be 1.28 D. The value of the dipole moment of phenetole, according to Li (30) (benzene, 25°C.) was stated as 1.0 D. The dipole moments of 2-vinyloxyethoxybenzene and 2-ethyloxyethoxybenzene, determined in this investigation (benzene, 30°C.) were found to be 1.78 D and 1.91 D, respectively. They are of the same order of magnitude as the other values for unsubstituted phenyl alkyl ethers. The lower value for the vinyloxy compound could be due to a contribution of the ring form, similar to IV (p. 6) or to a contribution of the linear form, similar to III (p. 4). The infrared absorption spectrum of 2-vinyloxyethoxybenzene exhibits both of the two peaks at 1639 cm^{-1} and 1621 cm^{-1} , as well as showing no appreciable shift of the 8.32 micron (1199 cm^{-1}) peak, indicating that the ring form (IV) does not contribute to the structure of the compound; it is compatible with the linear form (III). On the other hand, a comparison of the ultra-violet

absorption spectra of the vinyloxy and ethoxy compounds shows a considerable shift in the short wavelength region, suggesting that there is a contribution of the ring form. That this shift is not due to a linear form contribution, and that the spectral shift is not due to the difference in the position of the absorption maxima of the vinyloxy group and the ethyloxy group, will be discussed in the following section. The interpretations of the various physical properties seem to give conflicting indications as to the structure of these compounds, and therefore no conclusions can be reached concerning an interaction of the type proposed in these compounds.

2. Aldehydes.--In 2-(2-vinyloxy)ethoxybenzaldehyde the ring is effectively prevented from being formed by the large amount of steric hinderance afforded by the ortho-aldehyde group. Thus only linear forms should contribute, and the physical properties of this compound and the physical properties of 2-(2-ethyloxy)ethoxybenzaldehyde should be somewhat similar. This prediction is borne out quite well by the physical properties that have been determined for these compounds. The dipole moments of 2-(2-vinyloxy)ethoxybenzaldehyde and 2-(2-ethyloxy)-ethoxybenzaldehyde are 4.69 D and 4.49 D, respectively, which represents a difference of only 0.20 Debye units and are somewhat similar to the values of the dipole moment of 2-methoxybenzaldehyde, reported by Curran (31) as 4.21 D (benzene, 25°C.) and by Lumbroso (32, 33) as 4.19 D (benzene, 20°C.).

The similarity in the physical properties of 2-(2-vinyloxy)-ethoxybenzaldehyde and 2-(2-ethyloxy)ethoxybenzaldehyde is also

displayed in their infrared absorption spectra. Thus the carbon-oxygen stretching absorption peak occurs at the same wavenumber in both the vinyloxy compound (1689 cm^{-1}) and the ethyloxy compound (1689 cm^{-1}). Also the infrared spectrum of the vinyloxy compound exhibits the two peaks at 1639 cm^{-1} and 1621 cm^{-1} , attesting to the fact that the ring form does not contribute to the structure of this compound. Thus the ultra-violet spectra of these two compounds would be expected to be quite similar. Inspection of Figure 2 (p. 41) shows this to be the case. Also the difference between the molar exaltation of 2-(2-vinyloxy)ethoxybenzaldehyde (2.20; Table 3, p. 62) and 2-(2-ethyloxy)ethoxybenzaldehyde (1.63; Table 4, p. 63) is only 0.57.

In 3-(2-vinyloxy)ethoxybenzaldehyde, while there is no steric hinderance to the formation of the ring, the contribution of a phenolic oxonium ion form, analogous to II (p. 4) is relatively minor, for the phenolic oxygen atom and the aldehyde group are not suitably located on the benzene ring as to be in mutual conjugation. The dipole moments of 3-(2-vinyloxy)-ethoxybenzaldehyde (3.13 D) and 3-(2-ethyloxy)ethoxybenzaldehyde (3.45 D), while not as similar as the previous compounds, differ by only 0.32 Debye units. Thus the other physical properties would be expected to be somewhat similar, as in the previous case.

The difference in the position of the carbon-oxygen stretching absorption peak of the aldehyde group in the infrared spectra of 3-(2-vinyloxy)ethoxybenzaldehyde (1695 cm^{-1}) and

3-(2-ethyloxy)ethoxybenzaldehyde (1701 cm^{-1}), 6 cm^{-1} , is close to the accuracy with which the spectral positions can be determined on the chart paper (plus or minus 0.01 microns; plus or minus 3 cm^{-1} in this range of wavenumbers). The infrared spectrum of the vinyloxy compound exhibits both of the absorption peaks at 1639 cm^{-1} and 1621 cm^{-1} and shows no appreciable shift in the peak at 1199 cm^{-1} (8.34 microns).

Inspection of the ultra-violet spectra of these compounds shows that, while there is a great deal of similarity in the spectra, a slight difference is becoming apparent in the short wavelength end of the spectra. The molar exaltations of these two compounds are nearly identical (1.38 and 1.35, for the vinyloxy and the ethyloxy compounds, respectively). In conclusion, it may be stated that the physical properties of 3-(2-vinyloxy)ethoxybenzaldehyde and 3-(2-ethyloxy)ethoxybenzaldehyde indicate that these two compounds probably have the same type of structure, with respect to the type of interaction postulated, and that the ring form of the type postulated could, at the most, have only a slight contribution in the structure of 3-(2-vinyloxy)ethoxybenzaldehyde.

In 4-(2-vinyloxy)ethoxybenzaldehyde, since the two substituents on the benzene ring are in a position para to each other, there is no steric hinderance to the formation of the ring, and the two groups are in conjugation. Thus, if the ring is formed as postulated, a considerable difference in the physical properties of 4-(2-vinyloxy)ethoxybenzaldehyde and

4-(2-ethyloxy)ethoxybenzaldehyde would be predicted. In considering the dipole moments of these two compounds, it is found that the dipole moment of the vinyloxy compound (4.08 D) is smaller than that of the ethyloxy compound (4.48D) by 0.40 Debye units. This is a reversal of the situation in the 2-(2-alkyloxy)ethoxybenzaldehyde series, where the moment of the vinyloxy compound was larger than that of the ethyloxy compound. This difference of 0.40 Debye units is greater than that in the preceding 3-(2-alkyloxy)ethoxybenzaldehyde series, and is certainly greater than the experimental error in the determination of these properties.

This apparently anomolous difference in the dipole moments of these two compounds may indicate that the postulated ring form has a significant contribution to the structure of 4-(2-vinyloxy)ethoxybenzaldehyde. If this is the case, a considerable difference would be expected in the position of the aldehyde carbon-oxygen stretching absorption peak in the infrared spectra of these compounds. The observed positions of this peak in the spectra of 4-(2-vinyloxy)ethoxybenzaldehyde (1704 cm^{-1}) and 4-(2-ethyloxy)ethoxybenzaldehyde (1692 cm^{-1} and 1686 cm^{-1} -- split from a central value of 1689 cm^{-1} -- which, incidently, is the position in both of the 2-isomers) differ by 15 cm^{-1} , a value which is greater than the error in the determination of the position of the peak.

Since both of the peaks at 1639 cm^{-1} and 1618 cm^{-1} are present in the infrared spectrum of 4-(2-vinyloxy)ethoxybenzaldehyde, the ring is obviously not formed to the exclusion

of the linear form. A semi-quantitative study was undertaken on the amplitude of these peaks. Since the spectra obtained were in per cent transmittance, the reciprocal of the transmittance values of the maxima were subtracted from the reciprocal of the transmittance values of an extrapolated base line. The ratio of the peak height in absorbance units of the 6.08 micron peak (1639 cm^{-1}) to that of the 6.18 micron peak (1621 cm^{-1}) in the same units was then calculated. This order was chosen for, to the extent that the ring would be formed, the 6.08 micron peak would diminish. This ratio was calculated for each of the three isomeric 2-vinyloxyethoxybenzaldehydes, and was found to be: 2-isomer: 0.553; 3-isomer: 0.512; 4-isomer: 0.394. Since it was concluded that in the case of the 2-isomer only the linear form was present, the fraction of the contribution of this form would be 1.00. Normalizing these ratios so that the ratio of the 2-isomer is 1.00, the following new ratios are obtained: 2-isomer: 1.00; 3-isomer: 0.942; 4-isomer: 0.713, which, when converted into per cent, become: 2-isomer: 100 per cent (linear form); 3-isomer: 94 per cent (linear form); and 4-isomer: 71 per cent (linear form).

The above study was admittedly only semi-quantitative; however, it indicates that, in the case of the 3-isomer, only about 6 per cent of the actual structure of this compound could be contributed by the postulated ring form. Thus it is not difficult to explain why the study of the physical properties of this compound failed to do more than indicate a possibility

of a small contribution of the postulated ring form. The prediction of this study of about a 29 per cent contribution by the postulated ring form to the structure of 4-(2-vinyloxy)-ethoxybenzaldehyde should be capable of verification (or at least support) by a study of the remainder of the physical properties of this compound.

A comparison of the ultra-violet absorption spectra of 4-(2-vinyloxy)ethoxybenzaldehyde and 4-(2-ethyloxy)ethoxybenzaldehyde (Figure 4, p. 43) shows a considerable shift in the position of the short wavelength peak. The position of the maxima in the ethyloxy compound is 197.0 millimicrons and that of the vinyloxy compound is 205.5 millimicrons, a shift of 8.5 millimicrons, a value considerably greater than the experimental error in the determination of the position of these maxima. Moreover, the shift is in the predicted (cf. p. 8) direction, indicating that, as far as this peak is concerned, at least, the vinyloxy compound is the lower-energy compound of the two. Finally, the molar exaltation of the vinyloxy compound (3.34) is about 28 per cent greater than that of the ethyloxy compound (2.61). It is interesting to note that the value of this increase in molar exaltation (28 per cent) is quite close to the per cent contribution of the ring form predicted in the "semi-quantitative study" (29 per cent).

In conclusion it may be stated that the study of the physical properties of 4-(2-vinyloxy)ethoxybenzaldehyde and 4-(2-ethyloxy)ethoxybenzaldehyde indicated that, for the most

part, these two compounds have the same type of structure, but that there probably is a significant contribution of the postulated ring form to the actual structure of 4-(2-vinyloxy)ethoxybenzaldehyde.

3. Styrenes.--The dipole moments of 4-methylstyrene (0.38 D) and 3-methylstyrene (0.36 D), determined by Evarard and Sutton (34), are so close to the value quoted for toluene (0.37 D) by Gould (35) that some authors (34) feel that the dipole moment of styrene, itself, within the limits of experimental accuracy, is indistinguishable from zero. Comparing this with the dipole moment reported (36) for benzaldehyde (2.75 D), it would be predicted that, if there were any contribution at all of an interaction of the type postulated, it would be of such minor importance as to cause differences in the physical properties of these compounds so small that they would approach the experimental error of these determinations. In as much as the physical properties of 4-(2-vinyloxy)ethoxybenzaldehyde gave the most indicative evidence for the existence of the postulated interaction, it would be expected that the greatest difference in the 2-alkyloxyethoxystyrenes in this investigation would occur in the 4-isomers.

The difference in the dipole moment of 4-(2-vinyloxy)ethoxystyrene (2.15 D) and 4-(2-ethyloxy)ethoxystyrene (2.08 D) is 0.07 Debye units. This value is approaching the experimental error of the determination and is too small a difference to use for even a qualitative study of an interaction of the type postulated. An inspection of the ultra-violet spectra of these

two compounds (Figure 7, p. 46) shows a small shift in the short wavelength end of the spectra. Although the shift is in the predicted direction (vinyl-oxy compound absorption maxima at longer wavelength), its value, 3.0 millimicrons, is approaching the accuracy with which the position of the maxima, especially somewhat "rounded" maxima, can be determined from the chart paper (plus or minus 0.5 millimicrons) and the accuracy of the instrument (same value). Thus it may be stated that, while only very qualitative conclusions may be reached concerning interactions in these compounds of the type postulated, the strongest contribution to the actual structure of any of these styrenes would probably occur in 4-(2-vinyl-oxy)ethoxystyrene, and even in this compound such a contribution would probably be extremely minor, if detectable.

4. Beta-Nitrostyrenes.--If a comparison, similar to that made between styrene and benzaldehyde, is made between the dipole moment of beta-nitrostyrene (4.51 D, benzene, 25°C.; 4.50 D, benzene, 25°C., 4.27 D, dioxane, 25°C.; reported by Vasil'eva et al. (37), Sutton et al. (38), and Goebel and Wenzke (39), respectively) and that reported for benzaldehyde (2.75 D) by Smyth (36), it would be predicted that the contribution of an interaction of the type postulated would be stronger in the more polar beta-nitrostyrenes than in the aldehydes.

Since the beta-nitrovinyl group would be expected to have even greater steric requirements than the aldehyde group, and since it was postulated that the steric requirements of the

ortho-aldehyde group in 2-(2-vinyloxy)ethoxybenzaldehyde prevented the formation of the ring and thus any contribution from an interaction of the type postulated, then it would be expected that there would be no contribution of this type in the structure of 2-(2-vinyloxy)ethoxy- β -nitrostyrene. Thus only the linear form should contribute to the structure of this compound and the physical properties of this compound and those of 2-(2-ethyloxy)ethoxy- β -nitrostyrene should be quite similar.

The dipole moments of the vinyloxy compound (5.81 D) and the ethyloxy compound (5.65 D) are actually quite similar, differing by only 0.16 Debye units, a difference even smaller than that encountered in the corresponding aldehydes. No reported values for the dipole moment of 2-alkyloxy- β -nitrosytrenes were found in the literature.

The infrared absorption spectrum of 2-(2-vinyloxy)ethoxy- β -nitrostyrene shows two peaks at 1631 cm^{-1} and 1605 cm^{-1} , as would be expected. Although these peaks are slightly shifted with respect to the positions of the corresponding peaks in 2-(2-vinyloxy)ethoxybenzaldehyde, this could well be due to the solvent effect. 2-(2-Vinyloxy)ethoxybenzaldehyde, being a liquid, had its infrared spectrum determined as a pure liquid; 2-(2-vinyloxy)ethoxy- β -nitrostyrene, on the other hand, being a solid had its infrared spectrum determined in carbon tetrachloride solution. Also, the position of the strong peak at 1198 cm^{-1} (8.35 microns) in the infrared spectrum of the beta-nitrostyrene is not significantly shifted from the "normal" position of 1202 cm^{-1} (8.32 microns).

On this basis it would be expected that the ultra-violet spectra of 2-(2-vinyloxy)ethoxy- β -nitrostyrene and 2-(2-ethyloxy)- β -nitrostyrene would be quite similar. An inspection of Figure 8, p. 47, shows that these two spectra are quite similar. The only physical property that was determined for these compounds that showed an anomolous discrepancy was the molar exaltation. The molar exaltation values for all three isomers of 2-ethyloxy-ethoxy- β -nitrostyrene were very high; therefore these values can only be used with great reserve. Thus it may be stated that 2-(2-vinyloxy)ethoxy- β -nitrostyrene and 2-(2-ethyloxy)ethoxy- β -nitrostyrene probably have the same type of structure and that an interaction of the type proposed does not have any significant contribution to the structure of 2-(2-vinyloxy)ethoxy- β -nitrostyrene.

3-(2-Vinyloxy)ethoxy- β -nitrostyrene has not been prepared as yet and thus no further discussion of this isomer is possible.

So far in this investigation, within any series of positional isomers, if the physical properties of any isomer have shown a deviation from those of the remainder of the series, suggesting the intervention of, and some degree of structural contribution from, an interaction of the type that has been postulated, this isomer has been the 4-isomer. This trend would not only be expected to be continued by 4-(2-vinyloxy)ethoxy- β -nitrostyrene, but also to be intensified. Thus it would be predicted that the postulated ring form, IV (p. 6), would show a stronger contribution to the structure of this compound than it has shown to the structure of any other.

The difference between the dipole moment of 4-(2-vinyloxy)-ethoxy- β -nitrostyrene (5.43 D) and that of 4-(2-ethyloxy)ethoxy- β -nitrostyrene (6.14 D) is 0.71 Debye units. This difference is even more significant than its value would indicate, for, as can be seen, the moment of the vinyloxy compound is the lesser, the reverse of the situation encountered in the 2-isomers (where the ring did not have a contribution). If this difference in the dipole moments of these two compounds signifies the contribution of the ring form to the actual structure of 4-(2-vinyloxy)ethoxy- β -nitrostyrene, as it suggests, the other physical properties should also show a difference between these two compounds.

The infrared spectrum of the vinyloxy compound exhibits only one peak in the range $1639\text{--}1618\text{ cm}^{-1}$, and this peak occurs at 1621 cm^{-1} (6.17 microns). The "normal" 8.32 micron peak has been shifted to 1193 cm^{-1} (8.38 microns), a shift of 9 cm^{-1} . A consideration of the physical properties of 4-(2-vinyloxy)-ethoxy- β -nitrostyrene that have been discussed up to this point would certainly suggest not only that the ring form has a significant contribution to the structure of this compound, but also that the contribution of the linear form is so small as to escape detection (no peak was present in the infrared spectrum of this compound at or near 1639 cm^{-1}). Final, confirmatory evidence would be expected from the remainder of the physical properties.

An inspection of the ultra-violet spectra of these two compounds shows that such is not the case, for the two spectra

are quite similar. Thus, independently considered, the ultra-violet spectra would indicate that the structures of the two compounds would be the same. The only explanation offered for the lack of confirmatory evidence in the ultra-violet spectra is that the change in the electronic structure of the vinyloxy compound by the proposed interaction produces a change in the position of a maximum that was outside of the region investigated.

Finally, a consideration of the values of the molar exaltation of these compounds shows that, even though the ethyloxy compound still has a much larger exaltation than the vinyloxy compound (13.94 to 8.24, a difference of 5.60), it was not as much larger than the vinyloxy compound as was the case in the 2-isomers (ethyloxy: 10.24; vinyloxy: 3.19, a difference of 7.05). In conclusion it may be stated that the dipole moment data suggest that there may be a contribution by the ring form present, the infrared data indicates that this is the only form present, and the ultra-violet data indicates that this form is probably not present, and the molar exaltation data indicates almost nothing. Thus, until further investigations can be carried out on these and related compounds, no definite conclusions can be reached concerning the structure of 4-(2-vinyloxy)ethoxy- β -nitrostyrene.

5. Other Compounds.--An investigation, very similar to this investigation, is presently underway, the objectives of which are the preparation and the determination of the physical properties of a third series of compounds. These compounds include:

4-(2-vinyloxy)-ethoxyacetophenone, 4-(2-vinyloxy)ethoxy- α -methylstyrene, 4-(2-vinyloxy)ethoxy- α -methyl- β -nitrostyrene, 4-(2-ethyloxy)ethoxyacetophenone, 4-(2-ethyloxy)ethoxy- α -methylstyrene, and 4-(2-ethyloxy)ethoxy- α -methyl- β -nitrostyrene. It is hoped that this investigation will finally give the conclusive evidence for the proposed interaction.

In conclusion one final note should be made concerning the 8.32 micron peak in the infrared absorption spectra of the 2-vinyloxyethoxybenzaldehydes (cf. p. 3). Since the infrared spectrum of 4-(2-ethyloxy)ethoxybenzaldehyde did not contain this peak, the 8.32 ± 0.02 micron peak can be unambiguously assigned to the (linear) vinyloxy group.

CHAPTER IV

SUMMARY

2-Vinyloxyethoxybenzene, 2-, 3-, and 4-(2-vinyloxy)-ethoxybenzaldehyde, 2-, 3-, and 4-(2-vinyloxy)ethoxystyrene, 2- and 4-(2-vinyloxy)ethoxy- β -nitrostyrene, 2-ethyloxyethoxybenzene, 2-, 3-, and 4-(2-ethyloxy)ethoxybenzaldehyde, 2- and 4-(2-ethyloxy)ethoxystyrene, and 2-, 3-, and 4-(2-ethyloxy)- β -nitrostyrene have been prepared. The dipole moment of these compounds has been determined. The infrared and the ultraviolet absorption spectra of these compounds have been obtained. The molar refraction and the molar exaltation of these compounds have been determined.

A study of the experimentally determined physical properties of these compounds has lead to the postulation of an electronic interaction, in the form of a non-bonded six-membered ring, similar to that proposed by Butler (40-42) and supported by Jones (43), Marvel (44), Field (45), and Schuller (46), among others. Cram and Kopecky (47) have also proposed an analogous type of interaction. Evidence for the contribution of this type of interaction to the structure of 4-(2-vinyloxy)ethoxybenzaldehyde has been gained.

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BIOGRAPHICAL SKETCH

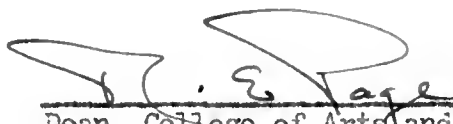
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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 11, 1962


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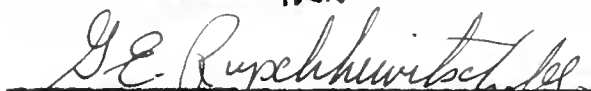
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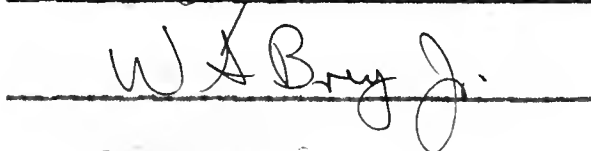

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